GASIFICATION OF OIL SANDS COKE

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SUMMARY

Coke derived from two Alberta oil sands operations has been gasified in a steam and oxygen blast using a 0.30-m diameter atmospheric pressure gasifier operated as both a fluidized and a spouted bed. Suncor coke crushed to an average size of 1.5 mm was treated in the spouted bed, whereas the 0.2-mm dia. Syncrude coke was gasified in fluidized beds of coarse sand, coke or dolomite. It was demonstrated that a strong gas of 8.4 MJ/m^3 heating value could be produced. H_2 and CO levels were about 39% and 20-30% respectively in the dry gas, with substantial levels of CO_2.

Carbon conversions varied between 20 and 94% depending on conditions. The effects of oxygen/coke ratio, rate of recycle of cyclone char, temperature and feed rate on gas heating value, carbon conversion, and efficiency were established. Results with Syncrude coke were somewhat poorer than with Suncor coke, particularly with respect to carbon conversion presumably due to the lower reactivity to steam, and the greater extent of carbon oxidation to CO_2. To achieve high carbon conversion and efficient operation with this coke, high efficiency cyclones and near complete recycle of char are required. Recommendations are made for changes to gasifier operation for this coke.

Potassium carbonate added in dry form was an effective catalyst, raising carbon conversion and steam decomposition while permitting operation at about 100°C lower than otherwise was possible. Dolomite beds effectively trapped sulphur emissions from the 6-7% S containing coke, yielding gases with sulphur levels <0.1%.

Heating values and hydrogen/carbon monoxide ratios in the product gases are readily predicted from a kinetics-free thermodynamic model.

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1. Introduction

Coke is produced as a by-product of the upgrading of oil sands of the Athabasca deposit. This material is partially used as a solid fuel in combustion, but a large amount is stockpiled due to its relatively high level of sulphur and other contaminants. The aims of this work were to assess cokes arising from two commercial oil sands plants, Suncor and Syncrude, as feed stocks for oxygen/steam gasification to produce either a clean burning fuel gas or a synthesis gas. Experiments were done in a 0.305 -m inside diameter atmospheric pressure gasifier located at U.B.C. which can be operated as a fluidized or a spouted bed.

The specific objectives of this contract can be summarized as follows:

(i) Assess the gasification characteristics of Syncrude and Suncor coke under various operating modes.

(ii) Investigate the effect of catalysts on the gasification of coke.

(iii) Determine if sulphur can be captured in-situ in the gasifier using suitable adsorbents.

(iv) Carry out three extended runs, at least one with each coke using a combination of best conditions from earlier tests.

(v) Continue work on mathematical modelling of gasifier performance.

(vi) Investigate the kinetics of coke gasification and sulphur capture in a small reactor.

The two cokes to be treated are produced in different ways and thus have different properties and size distributions. The Suncor coke is produced by delayed coking and hence is available in relatively large lumps. It is generally higher in volatile matter than Syncrude coke which is produced

in a fluid coker, and is of average particle size <0.5 mm. Samples of the two cokes to be evaluated were procured from their respective producers in northern Alberta. Proximate and ultimate analyses of the two cokes are given in Table 1. The volatile content of the Suncor coke sample at 11.9% is notably higher than the value of 6.9% for the Syncrude coke.

2.1 Gasification Pilot Plant

A schematic diagram of the gasifier is shown in Fig. 1. Table 2 lists some critical dimensions of the reactor system. The reactor itself consists of three major sections; the main body is a 10 gage carbon steel column with outside diameter 0.50 metres and height 1.37 metres, and is refractory lined to an inside diameter of 0.30 m to withstand the high temperatures. Below the main section is a 0.46 m high 316 stainless steel cone tapered at fifty degrees which is also refractory lined. The uppermost section of the reactor is a larger diameter (0.76 m) disengaging section, which reduces the amount of particulates leaving the gasifier.

The gasifier has been operated in both the spouted bed and the fluidized bed modes, depending on the size of the coke and/or the bed material. For fluidized bed operation, a distribution grid (see Fig. 7) is inserted between the main reactor section and the cone. This sieve-plate grid contains 2.5 mm diameter holes on a 2 cm x 1.73 cm pitch.

During the pre-heating stage of the experiment, hot gas enters the cone bottom and flows up through this grid, fluidizing and heating a pre-determined charge of bed material. This flue gas is generated in the propane burner, as shown in Fig. 1. For spouted bed operation the grid

TABLE 1: Analysis of Cokes Tested

	Suncor	Syncrude
Ultimate Analysis (Dry Basis)		
% C	84.9	79.49
H	3.93	1.56
N	1.32	1.69
S	6.02	6.96
Cl	0.01	0.70
Ash	3.09	8.30
O (Difference)	0.73	1.30
Proximate Analysis (As Received)		
% Moisture	1.80	3.73
% Volatile Matter	11.94	6.89
% Fixed Carbon	83.23	81.39
% Ash	3.03	7.99
Heating Value (Dry Basis) MJ/kg	34.7	29.7

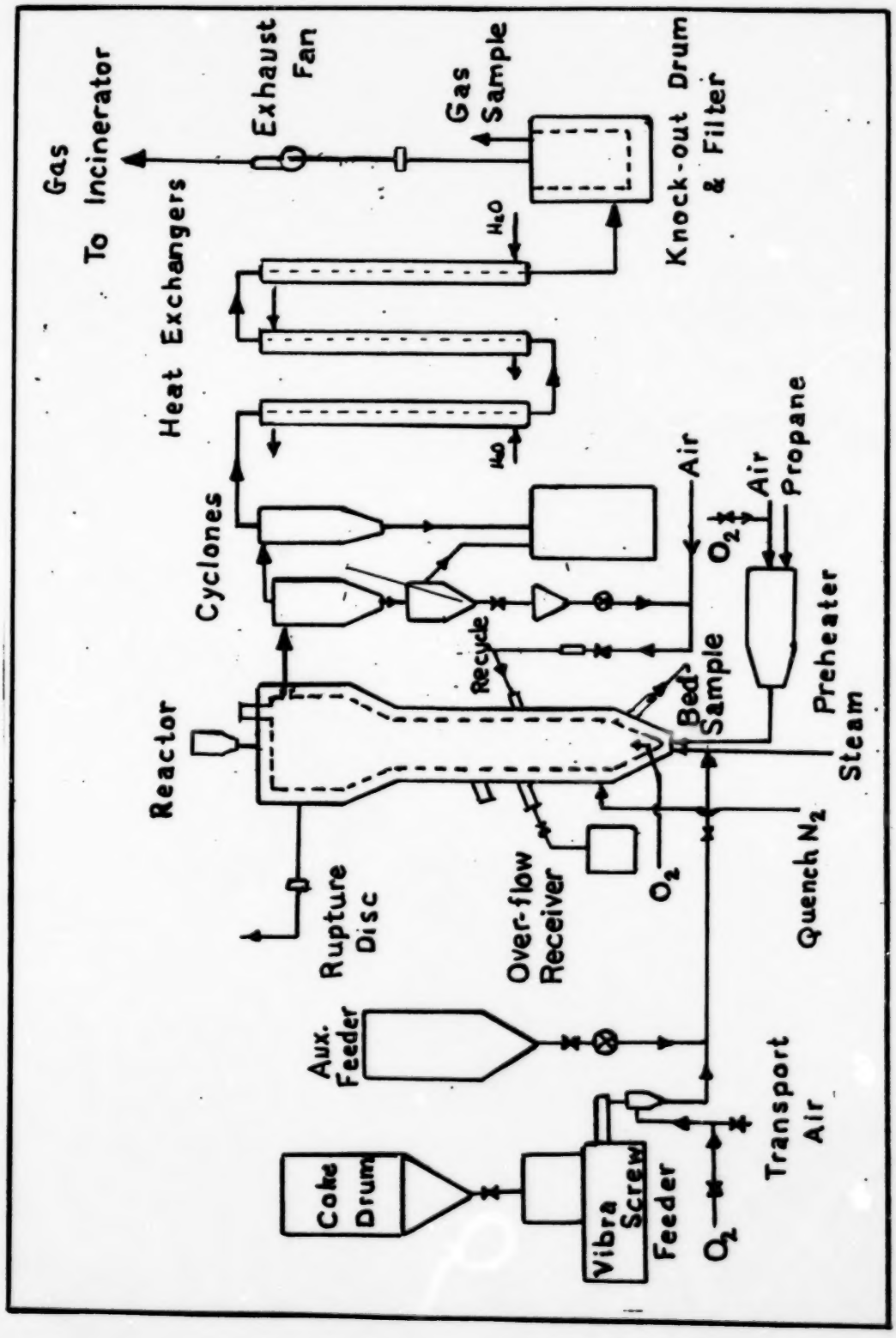


FIG. 1: Schematic Diagram of Gasifier Pilot Plant

TABLE 2: Gasifier Specifications

Gasifier:	
Column	0.50-m O.D. x 0.305-m I.D. x 1.37-m high
Cone	Angle 50°, height 0.46-m
Disengaging Section	0.76-m O.D. x 0.56-m I.D. x 0.61-m high
Spouted Bed Orifice Diameter	3.2 cm
Fluid Bed Distributor	Sieve plate type - 2.5 mm dia. holes on 2 cm x 1.73 cm pitch
Startup Burner:	176 kW max. propane fired
Cyclone - 1st Stage:	20.6 cm dia. x 27.3 cm cylindrical height x 33.7 cm cone height
Cyclone - 2nd Stage:	19.4 cm dia. x 26.7 cm cylindrical height x 48.3 cm cone height
Gas Coolers (3)	Each 2.2 m length x 7.6 cm I.D. x 10 cm dia. jacket
Gas Knock Out Drum	56 cm dia. x 90 cm height

is removed and bed solids are present in the cone section, where they are continuously spouted upwards from above the air inlet orifice.

Once the reactor has been heated to the desired temperature, coke is pneumatically transported from the vibra-screw feeder into the reactor via the 2.54-cm dia. solids transport line (Fig. 1). This line enters the cone section of the reactor and the coke exits at a point in the centre of the main body of the reactor approximately 8 cm above the grid in fluidized bed operation. It is also possible to feed a second solid material (either dolomite or potassium carbonate) into the solids transport line by means of the auxiliary feeder/rotary valve assembly.

During gasification, flue gas and some solids carry over from the reactor into the gas cleanup section. Particulate material is removed by two cyclones in series, and when necessary, dust can be recycled from the first cyclone into the reactor through a rotary valve. Char from both cyclones is collected in a char (dust) drum and weighed and analyzed following each experiment. Hot gas leaving the cyclones is cooled in an indirect heat exchange with water and any remaining dust is removed in a knockout drum and filter. The cleaned gas can then be sampled and analyzed before the excess is sent to a propane-fired incinerator located on the roof of the building.

2.2 Modifications to Gasifier Unit

Although the basic gasifier set-up was available at the beginning of this contract(1), a number of modifications had to be made for the gasification of oil sand cokes.

1. The original steel exhaust fan was corroded and a stainless steel one was built in the U.B.C. Chemical Engineering shops to replace it. A

mechanical seal was also installed to prevent corrosive gases escaping through the shaft hole to corrode the pillow blocks and cause premature bearing failure. An automatic lubricating system was installed on each pillow block to prevent the bearings running dry (Appendix A, Fig. A-1). This design evolved after our experience in operating the exhaust system on coal gas; a commercial unit with these features was not available.

2. An Apple II+ compatible computer was interfaced with the existing Doric 235 Data Logger to record the temperature readings on the gasifier. The hardware consists of the Doric 235 Datalogger and its corresponding remote Front End Modulator (FEM), RS232 connecting cable between the Doric 235 and the computer (Appendix A, Fig. A2), a super serial input/output card and the computer. The software consists of a controlling Applesoft program to acquire and process the temperature data. To date this unit has not been interfaced with the U.B.C. mainframe computer.

3. At the inlet to the spouted bed reactor, the original 2.54 cm S.S. flange was made to accommodate a shutter mechanism to prevent bed materials from dropping through the inlet bed orifice. Changes of start-up procedure and unacceptable gas leakage (particularly with H_2S present) necessitated construction of a new flange, without the shutter mechanism.

4. The S.S. pipe section between the propane preheating burner and the reactor inlet was burned through. A refractory-lined replacement was built and installed (Appendix A, Fig. A3).

5. Other modifications which were required specifically for catalytic gasification experiments, or to accommodate the fine particle size of the Syncrude coke are described in the discussion of those particular results.

3. Operating Procedure

Before the start of the gasification experiment the two gas chromatographs (one used for main gas constituents, the other for sulphurous species) are checked to ensure they are operating properly and if necessary they are recalibrated. The variou bottled gases, including propane, pure oxygen and quenching nitrogen, are then connected to their respective piping. Air from the building air compressor is fed to the inlet of the reactor, the coke feed line and the char recycle line to prevent them from being blocked with bed material. Depending on the experimental conditions, the bed material consisted of silica sand (16 mesh), dolomite (-18+50 mesh) or char. The initial static bed depth of a typical run is about 0.45 m and the bed material is charged from the top of the reactor. The reactor is then heated to 500°C using the propane fired preheater. The heating time varies from 1 hour for the char bed to 2 hours for the silica sand or dolomite bed. The bed is spouted or fluidized using air before the coke is blown into the reactor using pure oxygen. As the reactor temperature increases the propane to the propane preheater is decreased gradually and finally shut off when the temperature reaches 750°C. The spouting or fluidizing air is gradually replaced with saturated steam. At 0.5 hr after the introduction of coke, if desired, the char recycle system is turned on and the char is conveyed using air to the reactor. The reactor temperature is then controlled at the desired value by adjusting the steam and pure oxygen flow rates.

One hour after the start of the experiment, gas samples are taken at 20 minute intervals and analyzed for H_2, CO_2, O_2, N_2, CH_4, CO, H_2S and SO_2 using gas chromatographs. Any in-bed kinetic gas sampling begins when the reactor temperature is steady, which is about 2 hrs into the run. The temperatures pressure and various flowrates of the gasifier system are also recorded at

the same times as the gas is sampled. A typical experiment lasts from three to five hours to ensure that a steady state gas composition is achieved. As will be shown below, even after several hours the temperature still increases, but very slowly. The thermal capacity of the upper part of the reactor is such that a long time is needed to reach thermal equilibrium for the whole reactor. The coke feed, pure oxygen, char recycle feed, air and steam are shut off at the desired time. To prevent any fire hazard the ball valves for the coke feed and char recycle lines are turned off (see Fig. 1). The reactor is purged with a short burst of nitrogen to remove any trace of oxygen from the reactor. All electrical power to the gasifier is turned off and nitrogen, pure oxygen and propane are shut off at their respective sources. The reactor is allowed to cool overnight.

The next day, the char collected by the cyclones is discharged from the bins and weighed. A sample is analyzed for carbon and ash content. The coke feeding system is cleaned and the weight of coke used during the experiment is determined. The dust filter is dismantled and cleaned for the next run. The reactor cone is lowered and the bed material is weighed. The carbon and ash content for the bed sample is also determined by a combustion test. Then the reactor cone is placed back into position for the next run. If the pressure drop during the experiment is excessive, (>124 kPa) then the piping in the system is checked and any blockages are cleaned in preparation for the next run. The data collected are processed using the computer program and the results are analyzed. Particle size distributions of the solids found in the bed, and the cyclone catch are determined by sieving. In certain cases the sludge from the dust filter is analyzed for ash, and carbon and its size distribution determined.

4. Calculations and Definitions of Terms

After all the data from the experiment are gathered, they are entered in the appropriate format for the material and energy balance computer program. The values reported in the summaries of results (Tables 3 and 4) are average values over the steady state portion of the experiment. The standard condition for the calculation is set at 1 atmosphere and 15°C. In Tables 3 and 4 the material input mass flow rates are expressed in kg/h. The coke rate, M_c, is reported both on a dry basis and on a moisture, ash, and sulfur free basis, whereas the char recycle M_R is assumed to be dry and contains only carbon and ash. The steam input rate, M_s, includes the live saturated steam and the moisture in the coke feed. The cyclone catch is assumed to contain carbon and ash only with the proportions determined by weight loss in combustion in a muffle furnace. The % carbon conversion is calculated as the percentage of the carbon input in the fresh feed that is converted into CO, CO_2 and CH_4. The % H_2O decomposition is the percentage of water input decomposed to form hydrogen gas. Gas yield is defined as the volume of sulfur free dry gas at standard conditions (1 atm, 15°C) produced by one kilogram of moisture, ash and sulfur free (MASF) coke feed. The gross heating value of the gas (G.H.V.) is the total combustible heats of H_2, CO, CH_4 and H_2S in the dry gas also at the standard conditions. The hot gas heating efficiency η includes the combustible and sensible heats of the wet gas mixture and is expressed as a fraction of the available heat in the coke feed, whereas the cold gas efficiency includes only combustible heat of the dry gas constituents.

5. Results and Discussion of the Experimental Program

5.1 Suncor Coke Tests

The test work on Suncor coke was done in the spouted bed mode. The bed material was either raw coke, devolatilized spent coke from a previous run or a mixture of the two. Data for all Suncor coke trials are given in Table 3. The feed coke was crushed and screened to the particle size given in Table 5, which shows a mean particle size of about 1.5 mm. Run conditions included operation with and without recycle of cyclone product, runs with K_2CO_3 catalyst added, and runs with dolomite injection to capture sulphur. Where recycle of cyclone product was carried out, air was used to convey the solids back into the bed. Thus the gas heating value was lowered by virtue of the nitrogen content of this air. It is anticipated that in a larger scale process, steam would be used for this purpose, with no detrimental effect on the gas heating value. Condensation precluded use of steam for this purpose in the pilot plant. In order to compare results with and without cyclone product recycle, gas heating value results are expressed on a dry nitrogen-free basis. However the values given in Table 3 include the nitrogen as measured.

Typical dry nitrogen-free gas compositions from the Suncor coke tests were around 33% H_2, 22-28% CO, and 38-44% CO_2. Carbon conversions were in the range 47-94% depending on conditions. Maximum heating values of the gas were about 8.8 MJ/m^3 (dry, N_2-free basis). Temperatures in the bed averaged 920-970°C, with most runs being carried out at about 930°C. The unit operated best at coke feed rates of around 22 kg/h. Figure 2 shows the results of a typical experiment. Generally the temperature increases slowly with time (10-15 K/h) which is attributable to the heat capacity of the upper parts of the reactor; these parts of the unit require many hours to reach a

TABLE 3: Summary of Results - Suncor Coke Gasification

RUN NO	INIT. BED MAT'L	INIT. BED WT. (Kg)	FINAL BED WT (Kg)	FEEDRATE * (Kg/h) ADD'L FEED	m_{a_2}	m_c^{ss}	m_{N_2}	m_3	m_{CO_2}	m_{a_2}/m_3	m_3/m_c	TEMP °C AVG	TEMP °C MAX	G.H.V. MJ/m³	GAS YIELD m³/Kg	GAS ANALYSIS (% Mol) H_2	CO	CO_2	CH_4	N_2	DRY) H_2S	SO_2	% C CONVERSN	CYCLONE CATCH Kg/h	CYCLONE CATCH % C	η_{cyc} (%)	% H_2O DECOMP	RUN DURAT'N hr:min
113	SUNCOR CHAR	17.91	53.17	-	21.54	37.22	0.0	33.02	-	0.58	0.89	919	940	8.39	1.40	36.94	16.96	40.09	4.16	0.72	1.11	0.020	46.82	23.24	79.08	46.97	33.08	3:07
114	SUNCOR CHAR	21.77	16.55	-	19.56	16.07	0.0	31.33	-	1.22	1.95	970	1047	8.09	1.71	33.54	24.16	38.15	1.29	0.68	2.14	0.031	60.42	6.36	91.20	85.04	31.87	5:00
115	SUNCOR CHAR	20.04	23.02	-	20.05	21.42	0.0	36.10	-	0.94	1.68	956	986	8.10	1.36	34.79	22.26	38.11	1.77	0.78	2.25	0.028	48.37	11.09	92.95	77.90	23.02	4:39
116	SUNCOR CHAR	37.38	35.00	-	20.54	19.55	0.0	37.84	-	1.05	1.93	934	962	7.75	1.65	36.41	22.02	38.01	1.80	0.76	-	-	56.36	8.55	93.22	86.52	23.97	4:34
117 †	SUNCOR CHAR	37.39	41.70	-	22.65	19.33	8.50	34.92	15.28	0.65	1.80	933	962	6.77	2.38	28.29	19.82	32.83	1.24	16.54	1.27	-	70.54	5.67	93.96	85.23	29.92	4:32
118	SUNCOR CHAR	32.73	38.07	DOL. 5.42	22.94	19.60	8.50	34.45	12.07	0.72	1.76	912	928	5.68	2.65	24.45	17.80	38.06	1.38	17.56	0.71	0.032	82.90	4.23	74.21	67.80	29.25	2:30
119	SUNCOR CHAR + DOLOMITE	36.19	42.84	DOL. 5.58	23.59	19.65	8.50	33.48	11.14	0.77	1.71	917	951	5.87	2.26	25.42	19.08	37.09	1.27	17.00	0.13	0.010	70.77	7.87	68.46	66.17	27.11	2:16
120	SUNCOR CHAR	43.64	49.20	DOL 8.37	23.89	20.36	8.50	35.48	8.67	0.82	1.74	937	962	6.33	3.00	27.63	20.80	35.27	1.16	14.76	0.35	0.014	93.76	1.94	53.28	78.74	37.80	5.20
121	SUNCOR CHAR + DOLOMITE	35.45	24.20	K_2CO_3 2.27	23.47	23.99	8.44	32.87	16.28	0.71	1.42	869	887	7.84	2.76	34.71	25.71	26.59	0.76	11.27	0.93	0.019	80.27	7.76	56.96	91.16	58.80	3:09
122 •	SUNCOR CHAR	35.17	34.20	-	23.50	21.08	8.50	39.55	16.27	1.12	1.88	775	905	7.64	3.13	33.48	23.30	29.65	1.45	11.99	1.27	0.0	92.65	6.36	81.54	83.06	38.35	2:00
137	SUNCOR CHAR	18.53	27.73	-	24.36	21.78	8.24	36.34	16.27	1.12	1.67	914	925	5.89	3.33	29.18	15.12	37.31	1.39	17.00			96.18	3.97	84.55	66.35	36.24	3:26
138	SUNCOR CHAR	27.61	54.43	-	23.50	20.74	7.89	39.59	16.27	1.13	1.91	943	947	6.55	2.78	32.42	19.69	32.40	0.93	15.35			81.03	6.95	93.00	81.13	30.18	8:00

‡‡ COKE FEED IN MOISTURE-ASH-SULFUR FREE (MASF) BASIS

† H_2S WAS DETECTED USING WET METHOD

†† ALL RUNS : SPOUTED BED GASIFICATION
MOISTURE CONTENT OF COKE = 1.80%
MEAN PARTICLE DIAMETER = 1.49 mm

• FEED MATERIAL WAS COKE COATED WITH 10% K_2CO_3 BY WEIGHT

TABLE 4: Summary of Results - Syncrude Coke Gasification

RUN NO	INIT. BED MAT'L	INIT. BED WT. (Kg)	FINAL BED WT (Kg)	FEEDRATE (Kg/h) ADD'L FEED	m_a	m_c^*	m_{N_2}	m_s	m_{ch}	m_o/m_f	m_s/m_c	TEMP °C AVG	TEMP °C MAX	G.H.V. MJ/m³	GAS YIELD m³/Kg	GAS ANALYSIS (% MOL) H_2	CO	CO_2	CH_4	N_2	DRY H_2S	DRY SO_2	% C CONVER'N	CYCLONE RET'N Kg/h	CYCLONE RET'N % C	$\eta_{CYCLONE}$ (%)	% H_2O DECOMP	RUN DURAT'N hr:min
123	SILICA 16	40.00	38.60	–	23.84	22.13	10.95	45.27	19.32	1.08	2.04	960	973	3.47	0.94	17.53	8.71	44.20	0.22	27.23	0.78	1.33	32.36	16.47	90.30	43.21	6.68	3:19
124	SILICA 16	40.45	60.63	–	20.69	27.59	6.10	39.82	37.00	1.18	1.44	856	858	4.40	0.43	23.29	10.15	49.65	0.51	11.54	0.59	4.24	22.58	23.09	90.10	40.30	8.81	3:00
125	SILICA 16	42.16	39.89	–	18.67	22.05	0.0	45.22	–	0.85	2.05	936	945	5.23	0.92	25.06	10.93	53.19	0.25	1.18	5.92	3.47	37.17	15.58	89.93	60.69	9.29	4:14
126	SILICA 16	40.80	64.80	–	20.66	26.57	0.0	33.27	–	0.78	1.25	911	918	6.20	1.11	34.06	16.77	44.04	0.36	2.98	1.59	0.19	38.79	18.32	91.50	56.07	9.28	4:00
127	SILICA 16	35.68	38.07	K_2CO_3 2.26	22.86	18.31	0.0	39.59	=	1.25	2.16	957	998	8.38	2.58	37.61	23.93	35.80	0.0	0.0	3.06	0.01	79.68	5.13	81.18	82.56	33.64	3:81
128	SILICA 16	40.45	56.00	K_2CO_3 1.73	24.01	26.74	7.65	36.53	27.27	0.90	1.36	872	877	7.20	2.79	32.82	20.04	29.77	0.12	13.45	3.74	0.05	80.22	7.67	84.00	75.63	46.09	4:00
129	SYNCRUDE CHAR	34.54	17.61	DOL. 8.6	24.45	21.52	8.34	40.76	27.27	1.14	1.89	979	988	3.56	1.83	18.26	10.59	48.12	0.09	22.85	0.07	0.01	57.04	8.55	87.40	39.91	11.28	3:05
130	DOLOMITE/ CHAR	68.96	35.00	DOL. 2.0	23.20	36.01	8.33	36.77	29.82	0.64	1.02	901	902	5.24	0.85	27.60	14.41	44.47	0.23	15.08	0.26	0.003	30.22	26.11	86.00	36.98	18.31	4:10
131	DOLOMITE	42.61	34.32	DOL. 2.8	22.20	17.56	7.59	36.30	29.82	1.26	2.06	930	943	4.13	3.80	21.25	10.70	47.17	0.31	19.71	0.25	0.02	53.36	7.77	75.61	54.39	13.09	3:00
132	DOLOMITE	42.39	26.22	DOL. 2.8	22.41	15.18	7.64	37.70	29.82	1.48	2.48	914	924	3.24	1.58	18.83	7.56	51.62	0.34	22.72	0.05	–	48.98	7.30	72.22	62.64	7.26	4:00
133	DOLOMITE	37.62	62.38	DOL 5.37	22.22	19.45	7.68	42.33	–	1.14	2.17	1025	1033	0.84	0.58	5.08	1.78	65.78	0.0	27.30	0.03	0.03	20.88	19.60	62.38	8.52	0.92	4:00
134	DOLOMITE	43.64	18.07	DOL 6.95	25.43	25.88	15.27	47.92	–	0.98	1.85	1036	1059	1.51	1.50	9.12	3.70	67.41	0.0	20.15	0.02	0.00	57.77	16.36	66.00	14.50	5.04	4:00
135	DOLOMITE	38.64	46.36	DOL 6.80	23.48	29.41	9.37	39.32	29.82	0.80	1.34	940	950	4.42	1.74	23.19	12.80	44.32	0.33	19.34	0.006	0.00	55.45	20.87	67.65	35.30	20.68	8:00
136	DOLOMITE	40.82	28.68	DOL 3.52 H_2O 3.12	23.77	22.36	9.11	38.38	29.82	1.06	1.72	858	872	6.50	2.83	33.14	20.43	32.47	0.06	13.90			80.54	12.04	60.35	79.35	37.96	5:20

ALL RUNS: FLUIDIZED BED GASIFICATION
MOISTURE CONTENT OF COKE = 3.73%
MEAN PARTICLE DIAMETER OF COKE = 0.20 mm

* MASF BASE

TABLE 5: Particle Size and Hydrodynamic Parameters for Suncor Coke Gasification

Feed Coke			Bed Material			Cyclone Product		
Screen No.	Avg. Opening (mm)	Wt. %	Screen No.	Avg. Opening (mm)	Wt. %	Screen No.	Avg. Opening (mm)	Wt. %
+4	476	0.09	-4+8	3.57	4.02	+45	0.354	9.64
-4+8	3.57	49.0	-8+12	2.03	5.35	-45+60	0.302	4.02
-8+12	2.03	11.6	-12+16	1.44	16.23	-60+70	0.230	10.06
-12+16	1.44	11.2	-16+20	1.02	29.66	-70+80	0.194	5.11
-16+20	1.02	9.1	-20+30	0.72	28.25	-80+100	0.163	6.95
-20+30	0.72	4.5	-30+45	0.47	11.05	-100+230	0.106	54.82
-30	0.60	14.6	-45+80	0.26	4.08	-230	0.063	9.41

$d_p = 1/\Sigma(x_i/d_i) = 1.49$ mm $d_p = 0.76$ mm $d_p = 0.122$ mm

ρ_p 1230 kg/m^3

ρ_{bulk} 700 kg/m^3

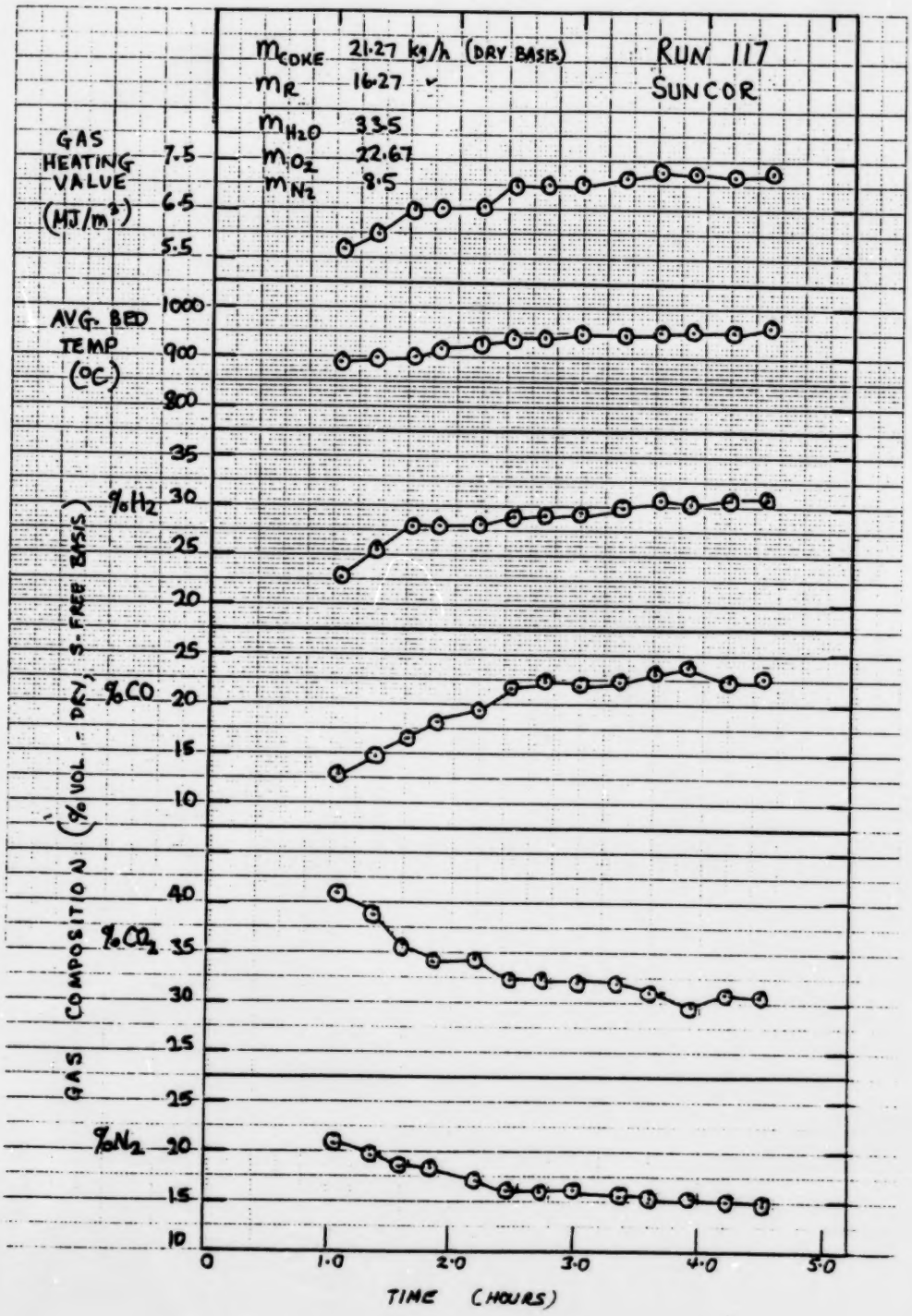


Fig. 2 Typical Result of Spouted Bed Gasification Run

thermally steady state. However the gas heating value, gas yield and carbon conversion are essentially constant after the first 2.5 hours of operation. As described in Section 4, the results in Table 3 represent averages over several hours of operation of data such as is shown in Fig. 2.

5.1.1 Runs Without Recycle, Sorbent or Catalyst

The initial series of four runs were done at different feed rates with no recycle from the cyclone product. The first run at a feedrate of 37.2 kg maf coke/hr resulted in a bed buildup of about 11.8 kg/h, i.e. the gasification rate was such that at a bed temperature of 920°C, the carbon consumption was below the carbon input rate and thus the bed depth increased. Also some pyrolysis of coke was occurring resulting in a high CH_4 content of about 4% in the gas. In subsequent runs the feed rate was dropped to about 20 kg maf coke/h, and at a similar oxygen rate, the bed depth remained uniform. Figure 3a shows that for these runs, as the coke rate went up, the heating value of the produced gas increased over the range 7.8 to 8.4 MJ/m^3, in spite of the corresponding drop in average bed temperature from about 970°C to below 920°C (Fig. 3b). The hydrogen content of these gases was 33.5-37%, CO from 17-22% while the CO_2 remained essentially constant at 39%. The carbon conversion

$$\%C \text{ conversion} = \frac{100 \times \text{moles } (CO + CH_4 + CO_2) \times 12}{\text{g C in feed}}$$

decreased as the feed rate increased (Fig. 3c) with typical values being 60% at the lowest feed rate, and 47% at the highest. With no recycle, the cyclone catch contained material of 91-92%C, which is clearly similar to the feed composition which suggests that attrited coke particles are blowing through the gasifier. Table 5 shows this material to be about 120 μm in

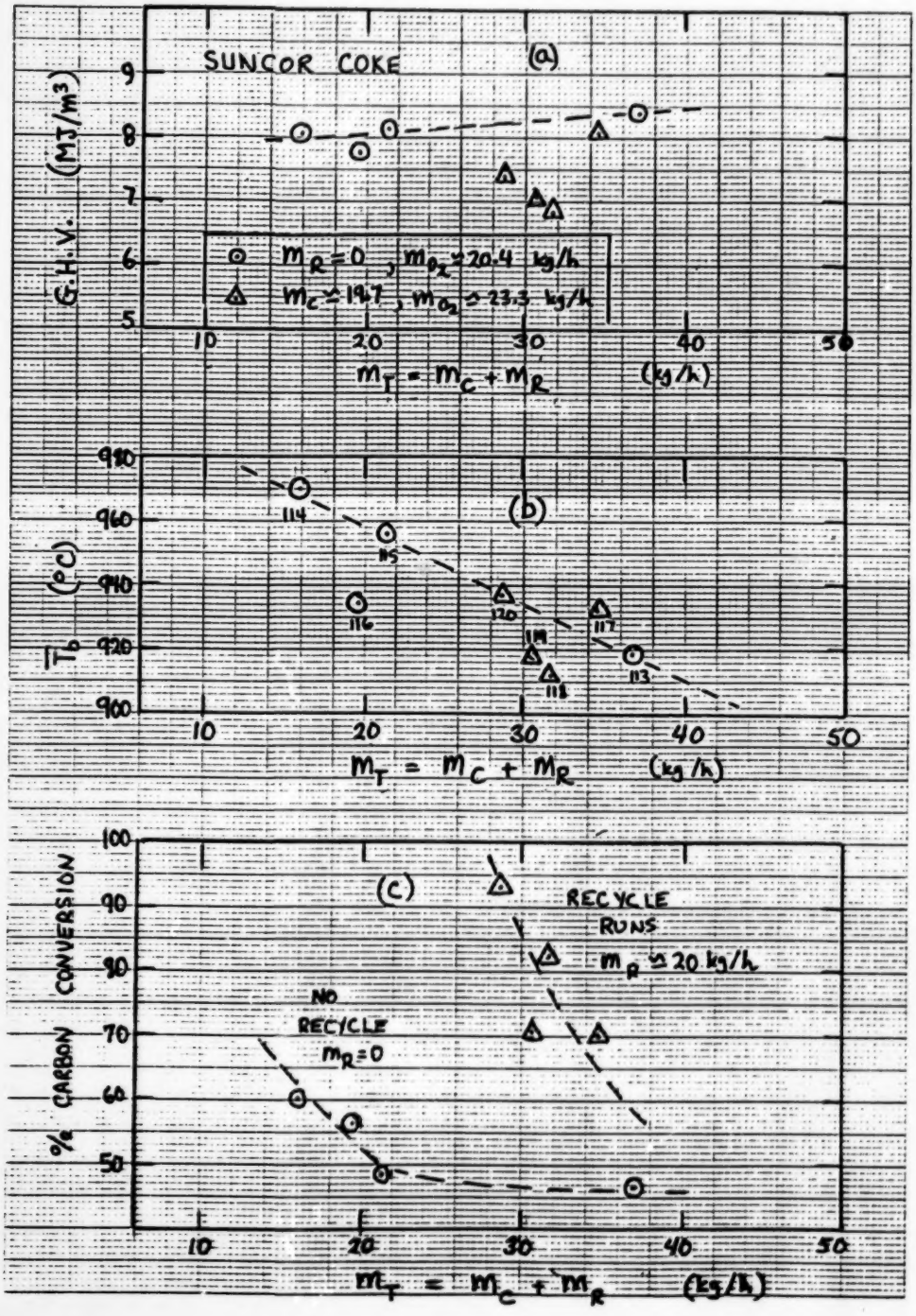


Fig. 3 Gas Heating Value, Average Bed Temperature and Carbon Conversion versus Total Fresh Coke + Recycle Coke Feedrate

mean size.

Operation with no recycle, and no sorbent or catalyst fed can thus be characterized as being relatively low in carbon conversion, but producing a strong gas with H_2/CO molar ratios of about 1.4, and high in H_2S at about 1.1 - 2.3% (Table 3).

5.1.2 Effect of Char Recycle

A set of four experiments (Runs 117-120) were carried out with recycle of the cyclone char. The char from the primary cyclone is metered through a rotary valve system and conveyed with air back into the gasifier. The use of this conveying air resulted in a N_2 level in the produced gases of about 17%. The conveying air carries in with it an extra 2.2 kg O_2/hr, such that with the pure oxygen rate being maintained at about 21 kg/h the total oxygen was about 10% higher than in the runs without recycle. The fresh coke rate was set at about 19.9 ± 0.7 kg/hr, and the recycle rate of the cyclone dust varied from 8 to 16 kg/h. Results are readily compared with the non-recycle runs by plotting against the feed rate as before, but including the feed per pass i.e. the sum of the fresh coke fed rate and the recycled char. Figures 3a to 3c show these results.

The gas heating value is expressed here in the plot on a N_2-free basis to compare with the previous results, although the uncorrected values are listed in Table 3. There is no trend of heating value versus total solids input (m_C+m_R), however as a group the data lie below those of the without recycle, perhaps due to the higher oxygen mass flow rate, since at a constant coke flow rate, the higher the oxygen flow the lower the gas heating value, at a given temperature. This is illustrated in Figure 4 which though

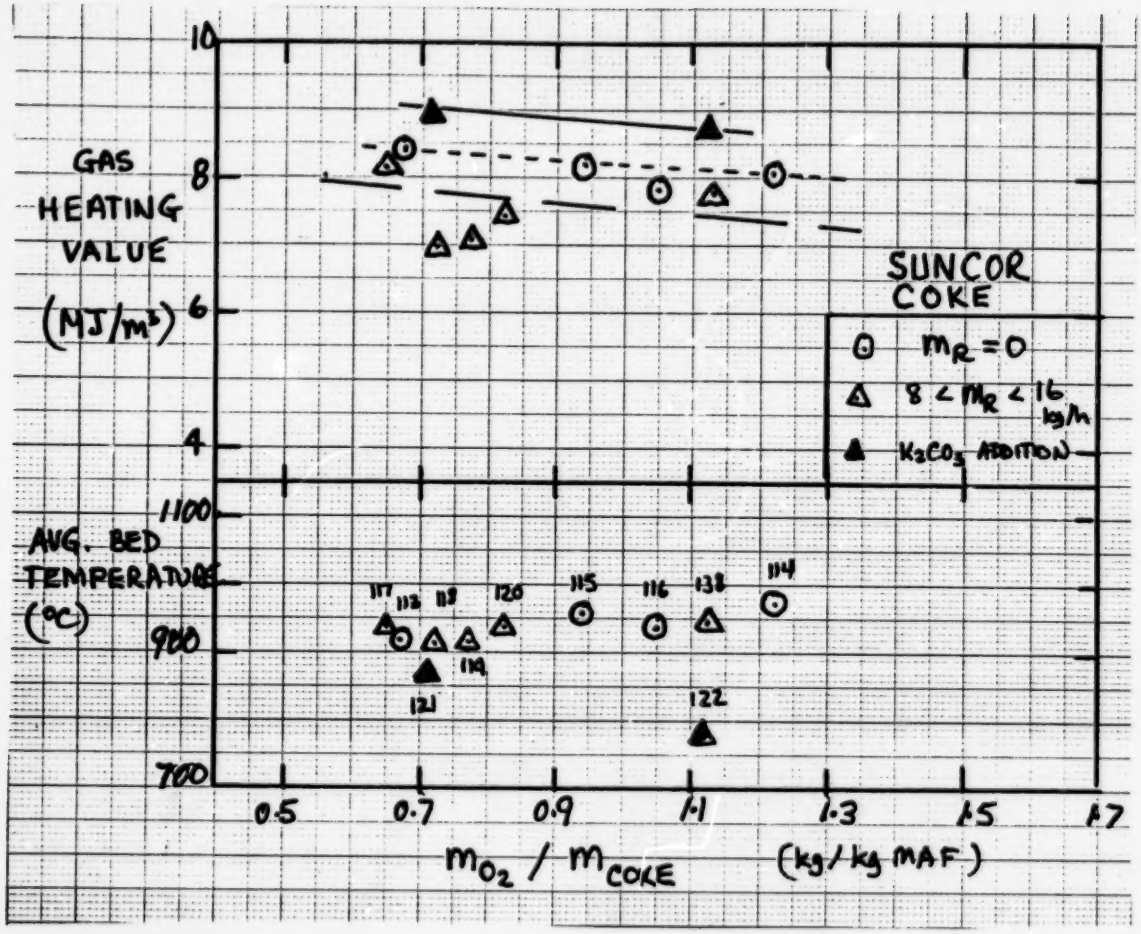


Fig. 4 Gas Heating Value and Average Temperature versus Oxygen/Feed Coke Mass Ratio

short in data illustrates the contours for heating value of the product gas. Figure 3b shows that as the total solids rate is increased there is a steady drop in temperature of the reactor. The carbon conversion data clearly show that an increase in the recycle improves the carbon conversion, with values typically of 55% with no recycle, going up to 70-90% depending on the recycle rate. In Fig. 3c, it should be noted that for all the recycle runs, $M_c \simeq 19.7$.

5.1.3 Dolomite Injection

The three recycle-runs were also fed with a small quantity of dolomite. Dolomite compositions are given in Appendix B. Co-addition of dolomite resulted in a decrease in the sulphur content of the gas to an average level of 0.5 ± .3% on a nitrogen-free basis, as compared to the value of 1.1 - 2.3%. Table 6 summarizes these results. The marked reduction in off-gas sulphur content is undoubtedly due to the reaction between H_2S and the calcined dolomite.

$$MgCO_3 \bullet CaCO_3 \longrightarrow MgO \bullet CaO + 2CO_2 \qquad (1)$$

$$MgO \bullet CaO + H_2S \longrightarrow MgO \bullet CaS + H_2O \qquad (2)$$

As subsequent work with Syncrude coke will show, better sulphur capture can be achieved by gasifying in a bed of dolomite rather than co-feeding small quantities of dolomite into a coke bed. The fact that only about 25-50% of the potential sulphur released is captured may be partly a contacting problem, as the small amount of available dolomite may not be in the H_2S releasing zones. A summary of the sulphur balances is given in Section 5.3.

If sulphur reacts only with the CaO and not the MgO as has been stated (2), then the sulphur loading will be 0.17 kgS/kg Dolomite. Thus 1 kg coke

TABLE 6: Dolomite Addition - Spouted Bed Gasification of Suncor Coke

Run No.	FEED RATE Coke* (kg/h)	Dolomite (kg/h)	Dolomite / Coke (kg/kg)	SULPHUR IN DRY GAS H_2S (%Vol)**	SO_2	MASS RATE OF SULPHUR Fed with Coke (kg/h)	Out with Gas
113	40.94		0	1.11	0.020	2.46	0.841
114	17.68		0	2.14	0.031	1.06	0.852
115	23.56		0	2.25	0.028	1.42	0.948
117	21.51		0	1.52	--	1.29	0.835
118	21.56	5.54	0.26	0.86	0.039	1.29	0.527
119	21.62	5.58	0.26	0.16	0.012	1.30	0.082
120	22.40	8.37	0.38	0.41	0.016	1.35	0.305

* Dry basis
** Dry, N_2-free basis
Note: Initial Bed 23-44 kg Coke (see Table 3).

TABLE 7: Catalyst Addition - Spouted Bed Gasification of Suncor Coke

Run No.	Coke* (kg/h)	K_2CO_3	T (°C)	G.H.V. (MJ/m^3)	Steam Decomposed(%)	%C Conversion	η Hot (%)	GAS COMPOSITION H_2	CO	CO_2	CH_4 (% vol)
117	21.51	0	933	8.11	23.8	70.5	76.3	33.9	23.8	39.3	1.5
118	21.56	0	912	6.89	24.59	82.9	66.1	29.7	21.6	46.2	1.7
121	24.07	2.3†	869	8.84	43.1	80.3	77.5	39.1	29.0	30.0	0.86
122	23.19	2.3††	775	8.68	38.9	92.6	96.0	38.1	26.5	33.7	1.68

* Dry basis
† Coated on coke
†† Dry feed

containing 0.06 kg sulphur requires about 0.35 kg dolomite. On the other hand if the magnesium is active as well, the dolomite demand will be about 0.18 kg/kg coke. In the current tests the dolomite loading was roughly 0.25 kg/kg coke, and averaging the results, the sulphur leaving with the gas was about 1/3 the level without the dolomite.

5.1.4 Catalysed Gasification

Two successful runs are reported with K_2CO_3 as catalysts for the gasification of the coke. Generally it was found that feeding coke coated with K_2CO_3 solution and subsequently dried, gave rise to considerable problems in the normal mode of feeding (Fig. 1). Six runs were attempted using two other feeding arrangements sketched below, with partial success using the method of Fig. 5b.

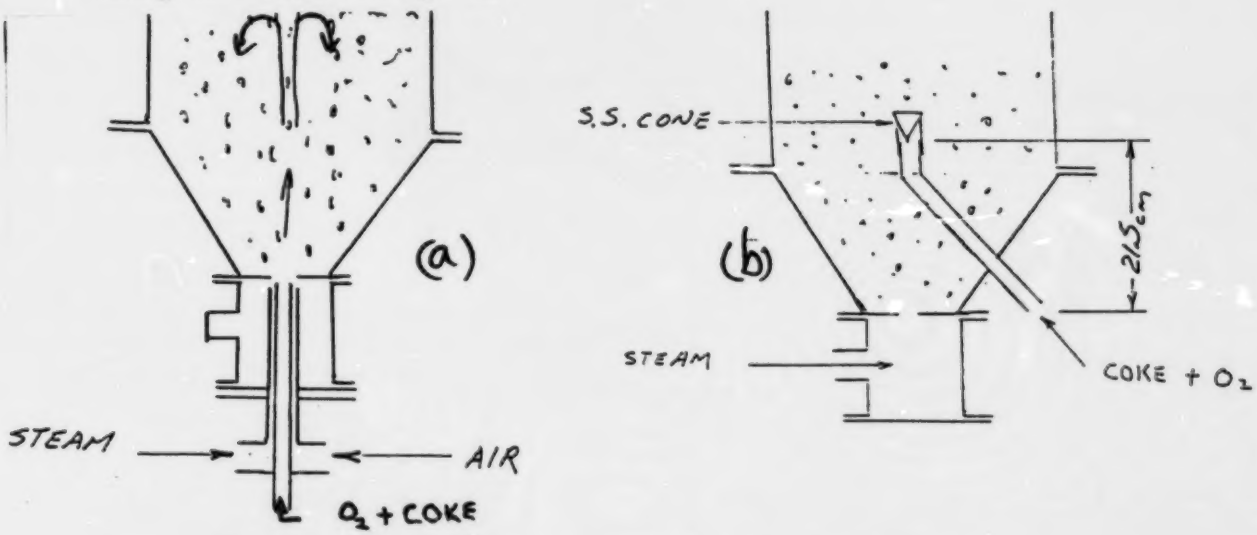


Fig. 5 Feeding Methods with K_2CO_3-coated Coke

Blockage was experienced with the method of Fig. 5a, whereas the method of Fig. 5b was successful in a short run. Dry catalyst was fed in a second

run whereby the problems of moisture adsorption onto the K_2CO_3 coated coal were eliminated entirely.

Runs with catalyst are compared in Table 7. These resulted in marked improvements as far as gas quality was concerned, giving the highest H_2 and CO levels, lowest CO_2 levels, little change in methane, and a 68% increase in steam utilization. Carbon conversions were generally higher. These benefits were achieved at temperatures of about 100°C lower than other comparable results, and at higher carbon throughput. A very interesting feature is that the potassium carbonate can be just as effective when added in a dry form rather than in the awkward and time consuming method of making up solutions, spraying onto the coal surface and drying, with all the above-described difficulties of feeding the resulting deliquescent solids.

5.1.5 Extended Run - Suncor Coke

One extended run of eight hours duration was carried out with Suncor coke. This run summarized in Fig. 6 and Table 3 consumed about 185 kg of coke. Generally the average bed temperature was very steady at 950°C after the first two hours. Since char recycling with air was used, the heating value was somewhat low at 6.6 MJ/m^3 with 15% N_2 content. On the N_2-free basis the heating value of the dry gas is 7.8 MJ/m^3. The heating value was steady after 3 hours, except for a small upset some 6.3 hours into the run. Operation was otherwise very smooth once the start-up period was over. The average gas composition on an N_2-free basis was then 38% H_2, 23% CO, 38% CO_2. Not shown in Figure 6 is the CH_4 content which averaged around 1% and decreased slowly over the course of the run.

This run illustrated the smooth operation typically found with Suncor coke.

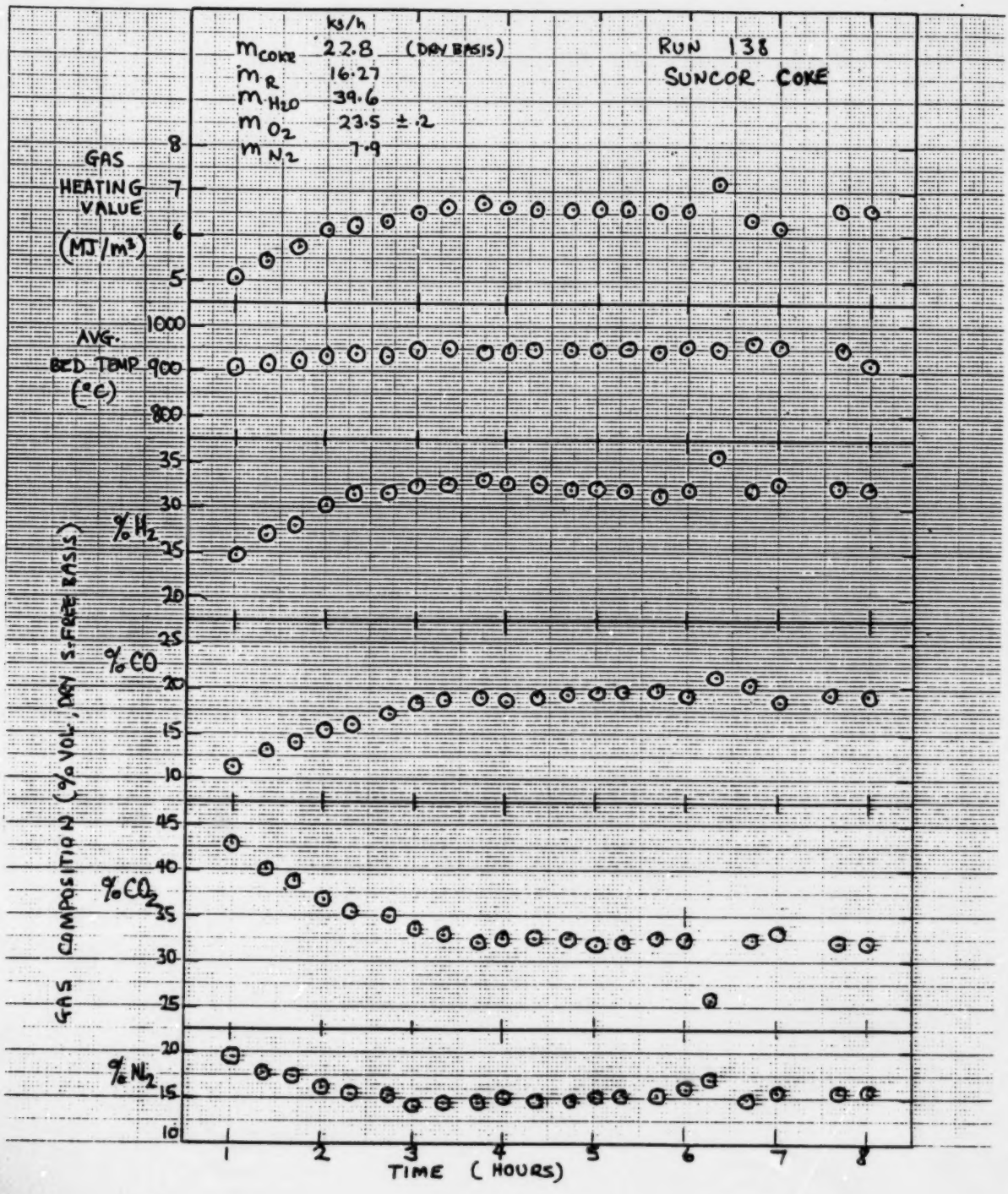


FIG. 6 Results of Extended Run on Suncor Coke

5.1.6 Overall Summary - Suncor Coke Runs

Suncor coke, being a delayed coke product and available in lump form could be crushed to a size convenient for spouted bed gasification. This coke was gasified over a range of temperatures, and a range of rates of feed, recycle, oxygen and steam. Gases typically were around 33-38% H_2, 22-28% CO,and 38-44% CO_2, with carbon conversions up to 94%. Maximum heating values of the gas were about 8.8 MJ/m^3 on a dry N_2-free basis. Hydrogen/carbon monoxide ratios in the product were typically 1.4. Potassium carbonate catalyst applied to the coke resulted in highest H_2 and CO levels, with corresponding lower CO_2 values, reflecting higher carbon conversions and markedly higher steam decomposition rates, at temperatures some 50-100°C lower than for non-catalytic runs. Co-feeding of dolomite resulted in a sulphur retention of about 25-50% at a low Ca/S mole ratio of 0.72.

5.2 Syncrude Coke Gasification Tests

The experiments with Syncrude coke were done in a fluidized bed as described in Section 2, and Fig. 7. The coke and its conveying oxygen were injected above the grid, thus the oxidation zone was not restricted to the first few cm. above the grid as might be expected if all the blast entered below the grid. In order to feed the Syncrude coke smoothly, a feed hopper with a sharper angle was used.

The small size of the coke (dp ≈ 0.2 mm - Table 8) gave a calculated minimum fluidization velocity of about 0.02 m/s. Three coarser materials were therefore used as bed material - silica 16 of dp ~ 1 mm, crushed dolomite of dp ~ 0.75 mm, and Syncrude coke dp ~ 0.2 mm. These materials have minimum fluidization velocities at temperature of about 0.4 - 0.8 m/s (Table 8). The gasifier was operated at superficial velocities in the range 1.3 - 1.8 m/s. These velocities are well above the terminal velocity of the Syncrude coke, so that the small coke particles tended to be blown through the bed and out of the gasifier. Thus recycle rates up to and exceeding the fresh coke rates were used. The runs were carried out with a blast of oxygen and steam, however for runs with recycle of cyclone dust, air was used to convey the cyclone product back to the bed, and hence nitrogen contents of about 13-27% (dry gas basis) appeared in the product. Steam rates were set in order to be able to fluidize the coarse bed materials, and to be able to control the temperature of the gasifier below 1000°C because of materials concerns. The experimental maximum bed temperature was 990°C, and typical values were about 930-950°C. This dictated the relatively high velocities of fluidization, and resulted in gases containing about 65-70% H_2O.

Because of the inefficiencies of the cyclone system which was not

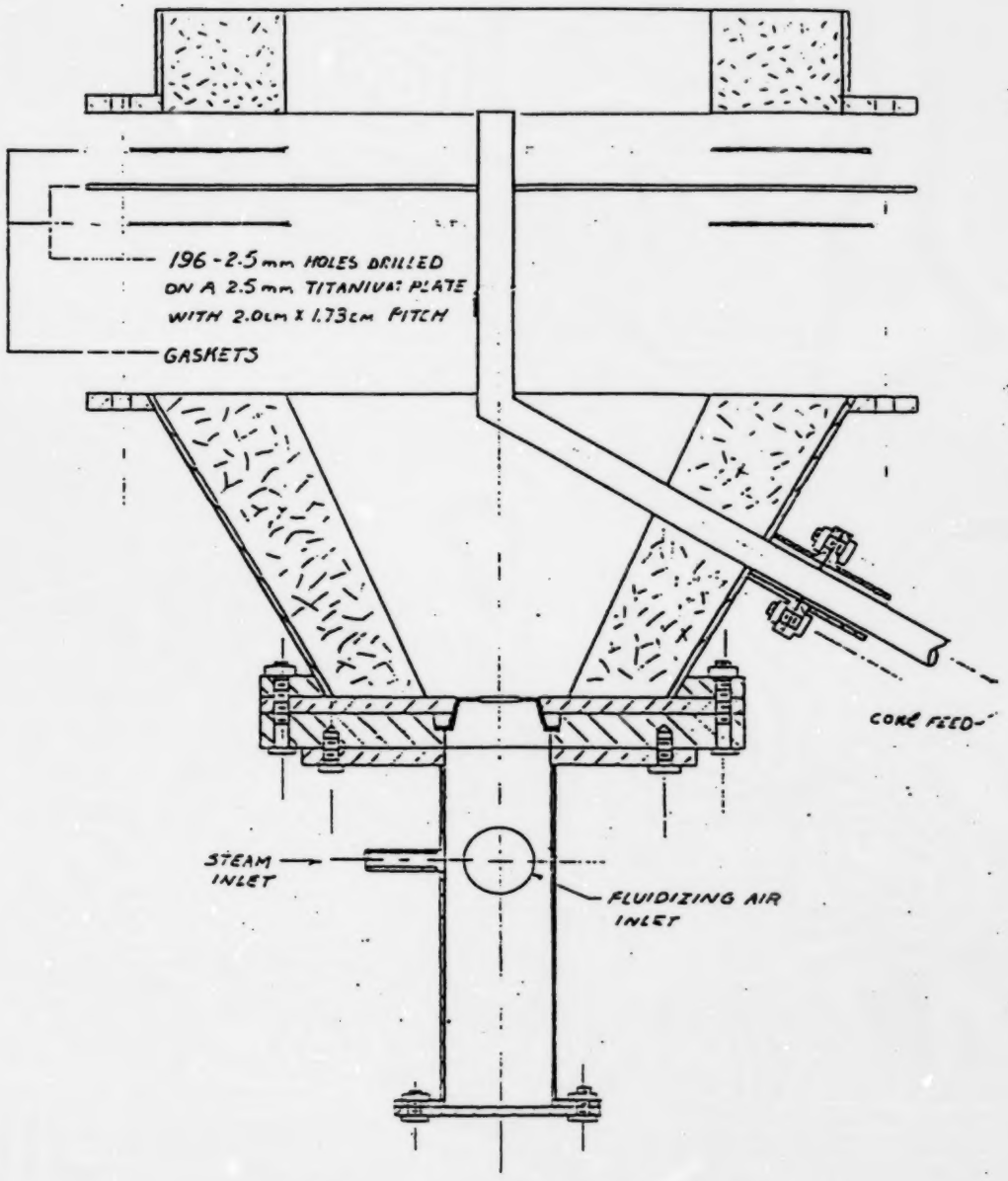


Fig.7 Distributor Plate Assembly for Fluidized Bed Operation

TABLE 8: Particle Size Distributions and Hydrodynamic Parameters for Syncrude Coke Gasification

Feed Material Syncrude Coke		Bed Materials** Silica 16		Dolomite	
Avg. Screen Size (mm)	Wt.%	Avg. Screen Size (mm)	Wt.%	Avg. Screen Size (mm)	Wt.%
0.710	2.97	2.03	0.47	1.190	0.29
0.475	5.91	1.435	31.24	1.016	38.72
0.302	17.44	1.016	49.71	0.718	50.88
0.214	51.57	0.718	15.00	0.475	9.08
0.163	9.09	0.595	3.58	0.302	0.28
0.106	12.04			0.214	0.14
0.063	0.98			0.177	0.60
$d_p = 1/\Sigma(x_i/d_i)$ (mm)	0.20	1.02		0.750	
ρ_p (kg/m^3)	1600	2.911		2.680	
ρ_b (kg/m^3)	1070	1330		1470	
U_{mf}*(m/s)	0.02	0.82		0.43	
U_t (m/s)	0.79				

$$1.31 < U_o < 1.8 \quad \text{(m/s at 900°C)}$$

* Calculated, at 900°C by method of Ref. 3.
** Syncrude Coke also used as bed material.

designed for high loadings of fine particles, the losses of carbon were high and the resulting carbon conversions low, even at essentially full recycle. On a dry gas-N_2 free basis, CO_2 levels in the gas were in the range 35-62%, reflecting a large extent of carbon oxidation. Hydrogen concentrations were typically 24-38%, and carbon monoxide 10-24%. The maximum heating values of the gas were 8.3-8.4 MJ/m^3 (dry, N_2-free basis). Figure 8 shows results for a typical experiment, and Table 4 summarizes the data for all runs.

5.2.1 Gas Heating Value

Heating value of the produced gases, which is proportional to the (H_2 + CO) content, expressed on a dry, nitrogen free basis is plotted versus the oxygen/fresh coke feed rate ratio in Fig. 9. Two separate curves are obvious which reflect to some extent temperature and feed rate effects. With no recycle of cyclone product, the heating value drops rapidly as oxygen/coke ratio exceeds 0.8, reaching a value of about 1.7 MJ/m^3 at O_2/coke = 1.0. At optimum conditions from a heating value prospect, O_2/coke ~ 0.7 kg/kg, which would give a heating value of 8-9 MJ/m^3. By means of the recycle, which effectively lowers the in-situ O_2/coke ratio, the heating value can be raised at a given input O_2/coke ratio. With the dry catalyst addition, heating values are about 8.3 MJ/m^3. The corresponding temperatures for these runs are also shown in Fig. 9. This plot is not shown to indicate a causal relationship as the oxygen/coke ratio does not in itself fix the temperature, because there is a large excess of steam added, some conveying air for recycle and variations in feed rate, all of which affect the ultimate reactor temperature.

Gas heating value can also be correlated with the feed rate at essentially fixed oxygen rate, as shown in Fig. 10. As the feed rate is

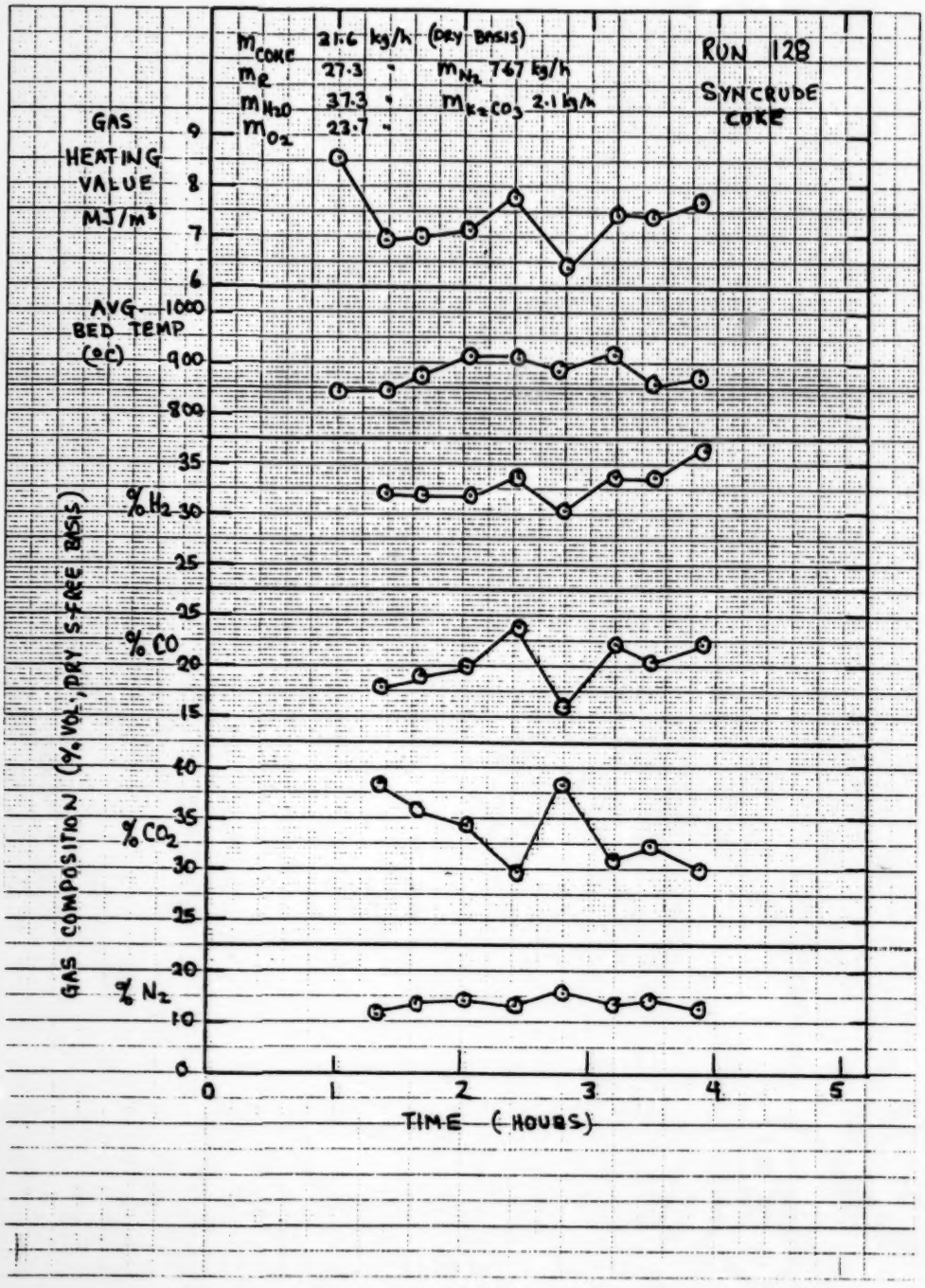


Fig. 8 Typical Result of Fluidized Bed Gasification Run

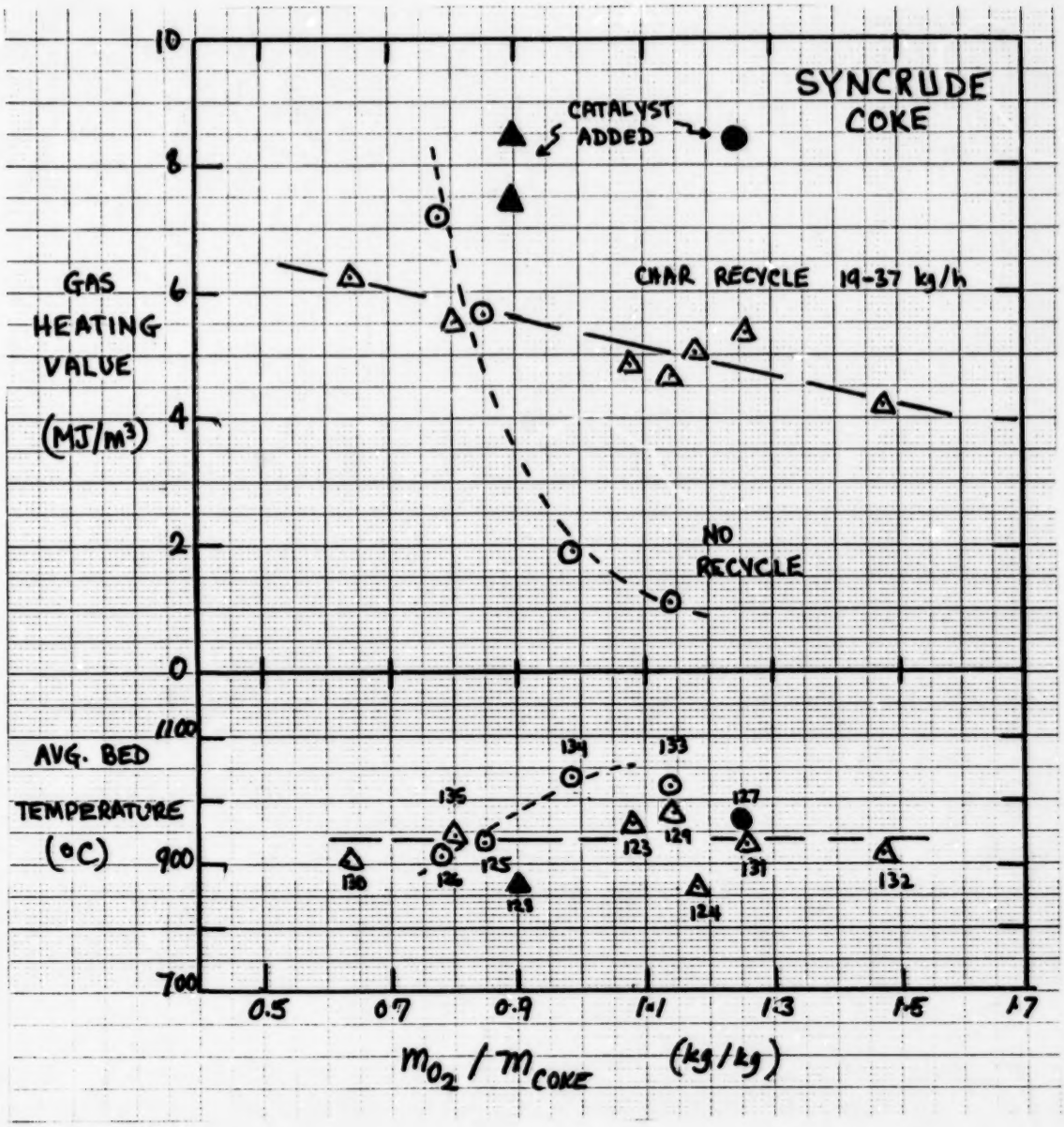


Fig. 9 Gas Heating Value versus Oxygen/Syncrude Coke Mass Ratio

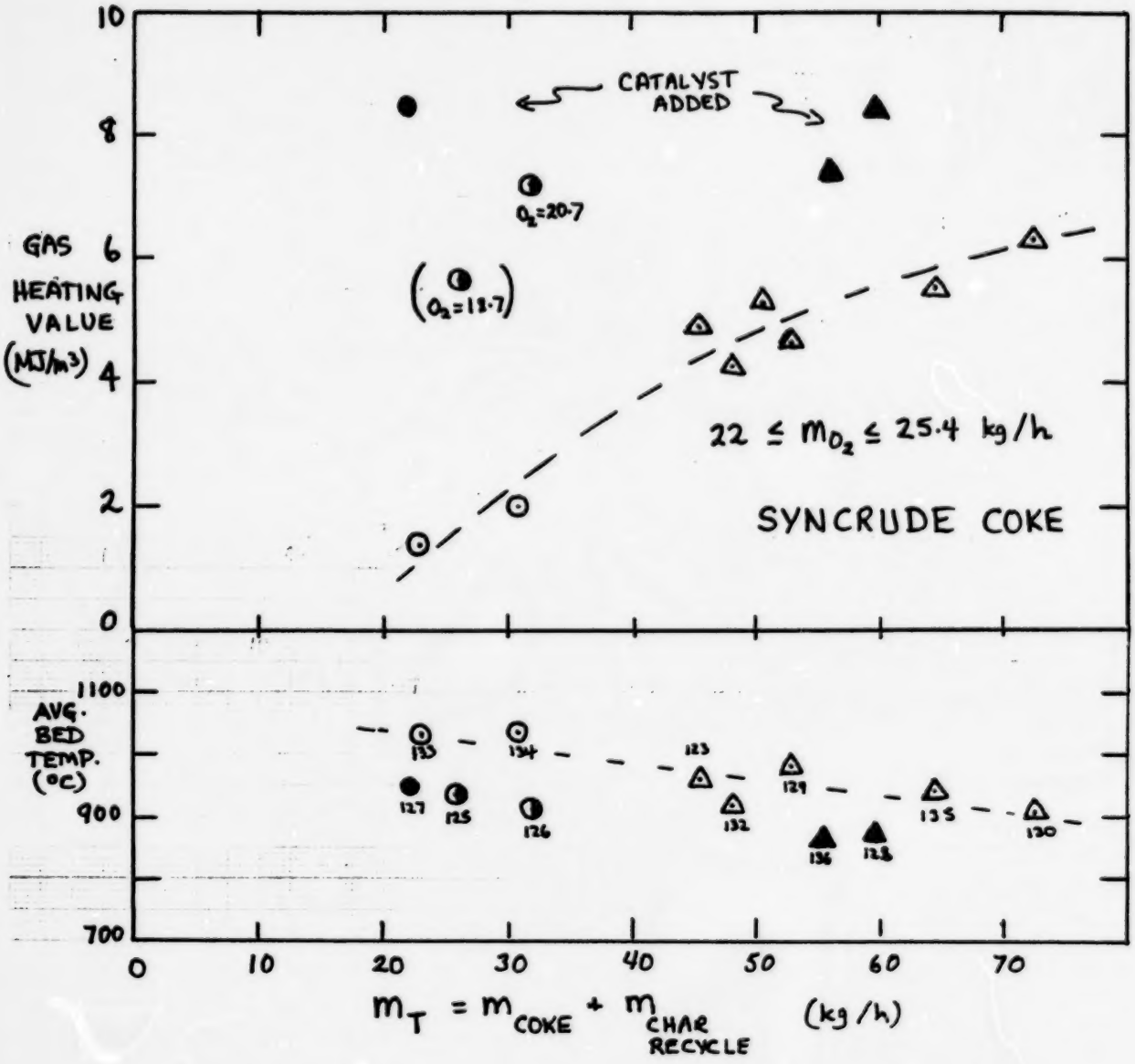


Fig. 10 Gas Heating Value versus Total Coke Flowrate for Syncrude Coke

increased at fixed oxygen rate, the O_2/coke feed ratio drops, and the heating value rises until a point is reached where the cooling effect on the bed quenches the reaction.

5.2.2 Effect of Cyclone Product Recycle

The effect of the recycle rate m_R on heating value at a fixed ratio of m_{O_2}/m_R is shown in Fig. 11, showing as expected an increase in heating values with recycle rate.

Another parameter of interest is the carbon conversion Fig. 12 shows the carbon conversion to be correlatable roughly with the bed temperature. In the absence of catalyst the carbon conversion at 900°C ≈ 40%, at 950° ≈ 60% when operated in the recycle mode. Without recycle, efficiency is lower at a given temperature.

5.2.3 Effect of Bed Composition

No marked effects on gas heating value are evident for changes in bed material from silica sand (Runs 123-126), to dolomite (Runs 130-135)(Table 3). There is a suggestion that Run 129A with a bed consisting of Syncrude coke, gives a slightly higher carbon conversion than the others.

5.2.4 Sulphur Capture

The effect of dolomite addition on the concentration of sulphur-containing species in the off-gas is marked. Table 9 summarizes the results. Although there is a good deal of variability in the data the average (H_2S + SO_2) levels for all runs without dolomite (discounting Run 125 which seems abnormally high), is 2.43%. For runs with dolomite addition,

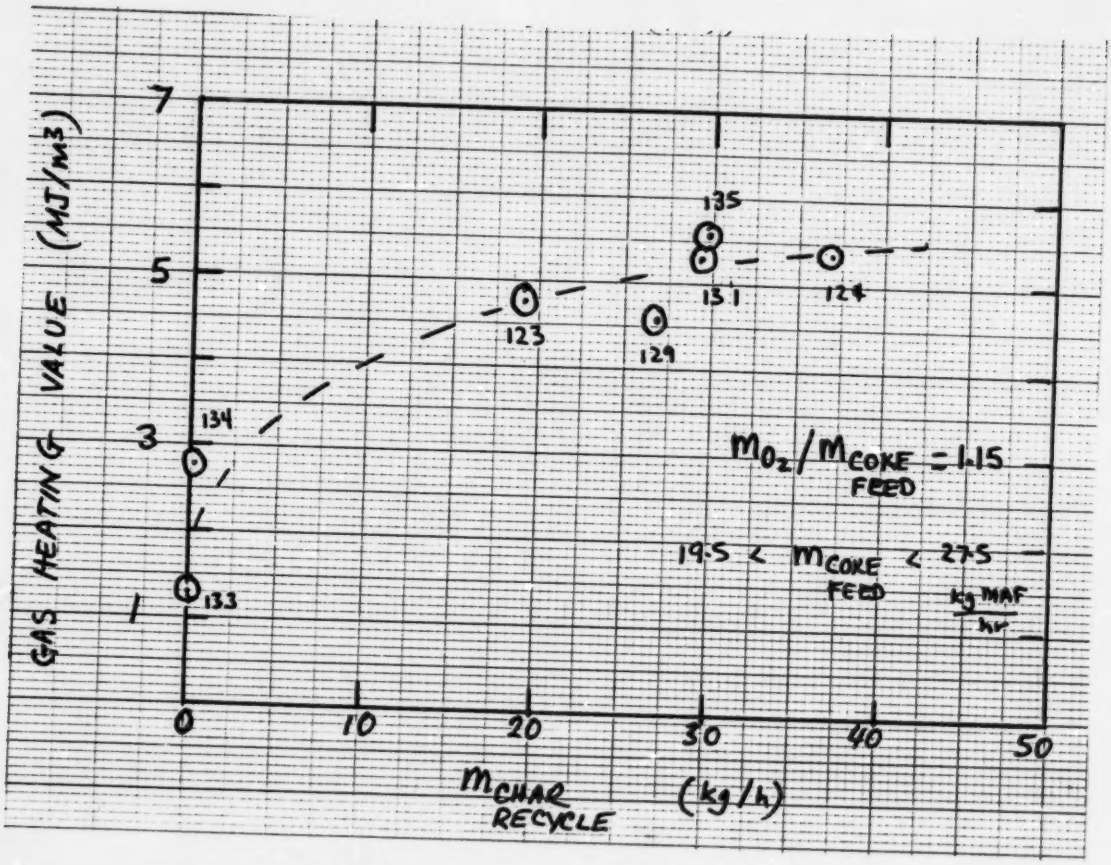


Fig. 11 Effect of Char Recycle Rate on Gas Heating Value for Syncrude Coke

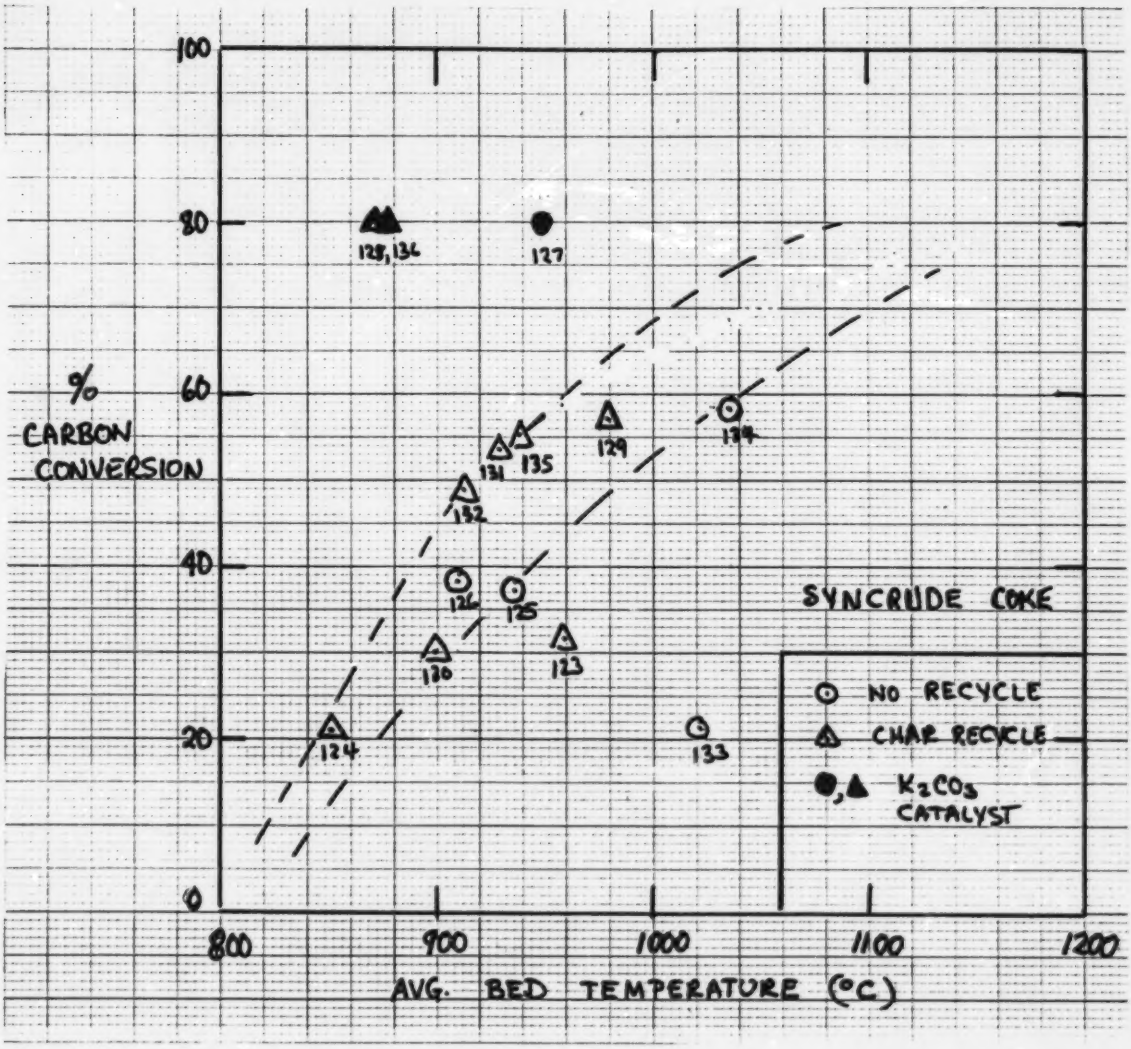


Fig. 12 Carbon Conversion versus Average Bed Temperature for Syncrude Coke

TABLE 9: Dolomite Addition - Fluid Bed Gasification of Syncrude Coke

Run No.	Initial Bed Material	Wt. (kg)	Feed Rate Coke (kg/h)	Char* (kg/h)	Dol. (kg/h)	Cumulative Ratio Dol./Coke (kg/kg)	Sulphur in Dry Gas H_2S (% vol.)	Sulphur in Dry Gas SO_2 (% vol.)	Mass Rate of Sulphur Fed with Coke (kg/h)	Mass Rate of Sulphur Out with Gas (kg/h)
125	Silica	42.5	26.1	-	-	0	5.99	3.51	1.83	2.72
126	Silica	40.5	31.5	-	-	0	1.64	0.20	2.21	0.76
133	Dol.	37.6	23.0	-	5.4	0.74	0.048	0.048	1.61	0.0097
134	Dol.	43.6	30.7	-	7.0	0.61	0.025	-	2.15	0.011
128	Silica	40.5	31.7	27.3	-	0	4.32	0.058	2.22	4.04(?)
123	Silica	40.0	26.2	19.3	-	0	1.07	1.83	1.83	0.63
124	Silica	40.5	32.7	37.0	-	0	0.67	4.80	2.29	0.82
129	Char	34.5	25.4	27.3	8.6	0.78	0.091	0.013	1.78	0.045
130	Dol.+Char	69.0	42.6	29.8	2.0	0.23	0.31	0.004	2.98	0.115
131	Dol.	42.6	20.8	29.8	2.8	0.84	0.31	0.025	1.46	0.258
132	Dol.	42.4	18.0	29.8	2.8	1.07	0.065	-	1.26	0.017
135	Dol.	38.6	34.8	29.8	6.8	0.33	0.0074	-	2.44	0.0044

* Recycled from cyclone.

the average level is 0.14% which suggests a sulphur capture of some 94%. As explained in section 5.1.3 the dolomite demand assuming only CaO reacts will be 0.21 kg dolomite/kg Syncrude coke. In all cases the dolomite available exceeded this amount (Table 9). In the best case (Run 135) the H_2S level in the off-gas is 74 ppm.

Examination of the results in Table 9 suggests some sulphur oxidation in Runs 123, 124 and 125 where SO_2 levels either exceed or are a substantial part of the H_2S levels. Dolomite was effective when added as feed to a fluid bed of coarse coke (Run 129). In most runs the initial fluid bed was made up of calcined dolomite, and an additional amount of dolomite was fed along with the Syncrude coke. There does not appear to be a correlation between the cumulative dolomite to coke ratio and the sulphur content of the gas. This is perhaps not unexpected due to the difficulties of the H_2S measurements at low concentrations, and the differences in gas yield, oxygen/coke ratio, temperature, etc. of the gasifier. In 5 of the 7 dolomite addition runs, total sulphur levels of below 0.105% or 1050 ppm H_2S and SO_2 were achieved, in contrast to the 24,300 ppm average without dolomite. It should be noted that the efficiency of sulphur capture will be a function of the surface area of the calcined dolomite which is not under the control of the experimenter. A separate investigation by Ph.D. candidate Q. Nguyen aims to quantify the factors affecting the sulphur capture (Section 5.5). Sulphur balances are discussed separately in section 5.3.

5.2.5 Catalyst Addition with Syncrude Coke

Results for two runs with K_2CO_3 addition are shown plotted with the other data in Figures 9-12. Compared to results without catalyst, catalyst

addition at 10 ± 2% loading on coke, results in substantially higher heating values (Fig. 9,10) and higher carbon conversion (Fig. 12), while operating at much reduced temperatures. It seems clear from Fig. 12 that to obtain carbon conversion in the range of 80% without catalyst would require temperatures in excess of 1000°C, while with catalyst, this level of conversion is attainable at about 875°C. The sulphur removal evident with the catalyst in this case appears surprisingly low. Dry feeding is a simple and effective way to add the catalyst. Utilization of the catalyst was not studied in these two tests. Table 10 compares runs with catalyst with those most similar in feed conditions. Of particular note are the substantially improved carbon conversions (~80% vs <50%), heating values (8.3 MJ/m^3 vs 6-7 on a N_2-free basis) % steam decomposition values (40% vs 16%).

While the use of catalysts appears to be strongly beneficial it is not altogether certain that a catalyst will be necessary under optimal conditions. Thus gasification at higher temperatures than practised here may be possible, resulting in high carbon conversions.

TABLE 10: Catalyst Addition - Fluid Bed Gasification of Syncrude Coke

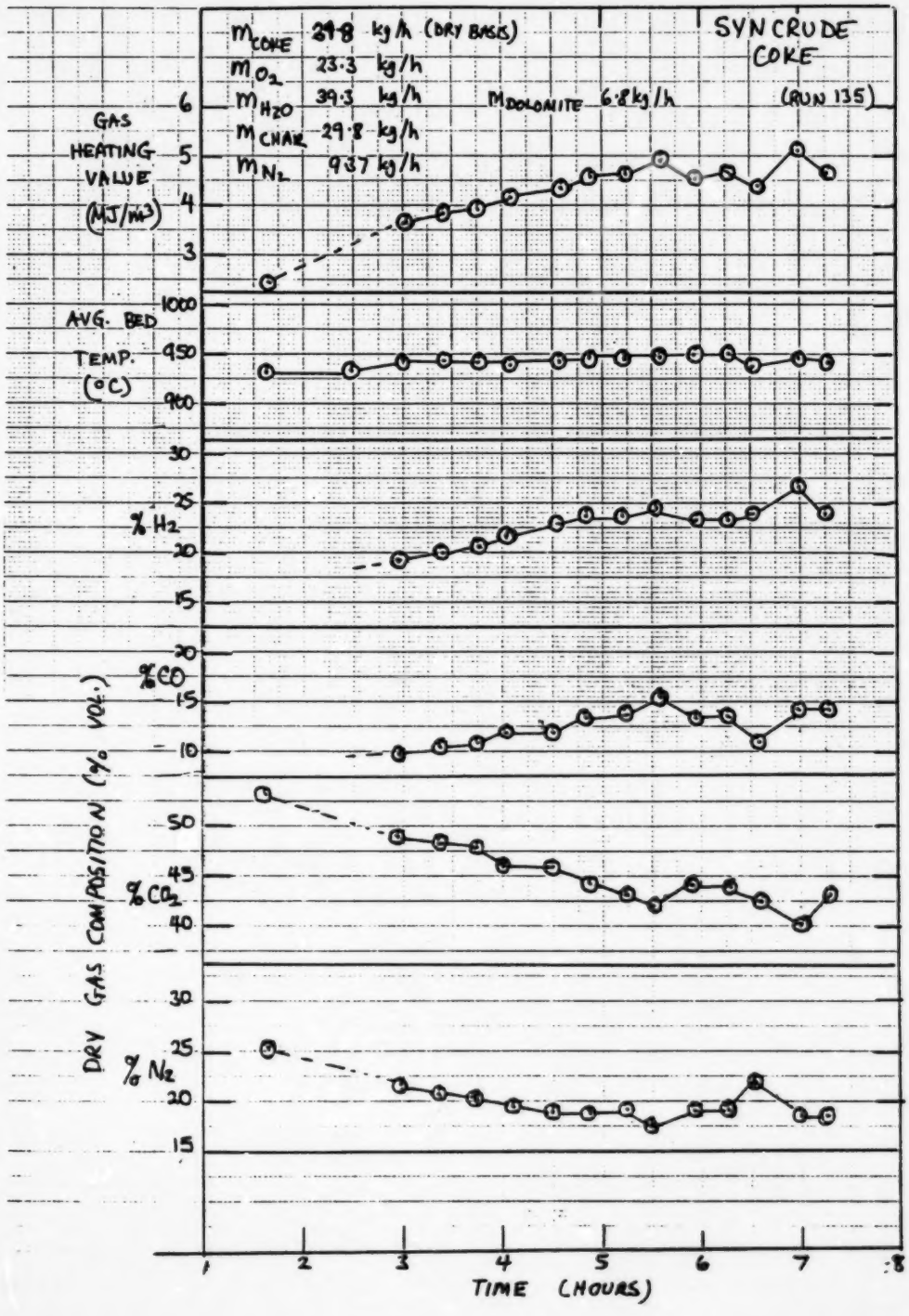
Run No.	Feed Rates (kg/h)+				Catalyst Load K_2CO_3/Coke (kg/kg)	T_b (°C)	G.H.V.* (MJ/m_3)	%C Conversion	$\%H_2O$ Decomposition	Gas Analysis*,† (% vol.)			
	Coke	O_2	Char	H_2O						H_2	CO	CH_4	CO_2
127	18.3	22.9	-	39.6	0.12	951	8.38	79.7	34.9	37.6	23.9	0	35.8
125	22.1	18.7	-	45.1	0.00	936	5.23	37.2	9.8	28.0	12.2	0.3	59.5
136	26.4	23.8	29.8	36.9	0.12	875±25	7.60	80.0	40	38.9	24.0	0.07	38.2
128	26.7	24.0	27.3	36.6	0.08	872	8.32	80.2	47	39.7	24.2	0.15	36.0
135	29.4	23.5	29.8	39.4	0.00	940	5.48	55.5	22	28.8	15.9	0.41	54.9

* N_2-free basis
† Sulphur-free basis
\+ Runs 136, 128, 135 also have N_2 flow

5.2.6 Extended Runs

Two slightly extended runs are reported. A series of feeding and downstream gas pipe blockage problems made these runs shorter than originally planned, and they were completed at the very end of the contract period. Run 135 (Fig. 13) ran for 8 hours at a high coke feed rate of 34.8 kg/h to give a total of 280 kg of dry coke fed. Although thermally the gasifier appeared steady at an average bed temperature of 940±5°C, the produced gas was high in CO_2 which declined over the first five hours after which all gas species and the heating value remained steady. The results from this run were normal in all respects, as seen in the plots of heating value versus oxygen/coke ration (Fig. 9), and total coke flow rate (Fig. 10). The carbon conversion was around 55% and some 143 kg of cyclone dust was recovered.

The final run undertaken on Syncrude coke lasted about five hours. This catalytic gasification run (Fig. 14) showed a constant gas heating value and constant gas composition after the first 2.5 hours, however a significant temperature cycle occurred during the run. The temperature rose from about 825°C to 920°C and appeared to be cycling downwards at the end of the run. The magnitude of this temperature cycle was unusual.



13 Results of Extended Non-Catalytic Run on Syncrude Coke

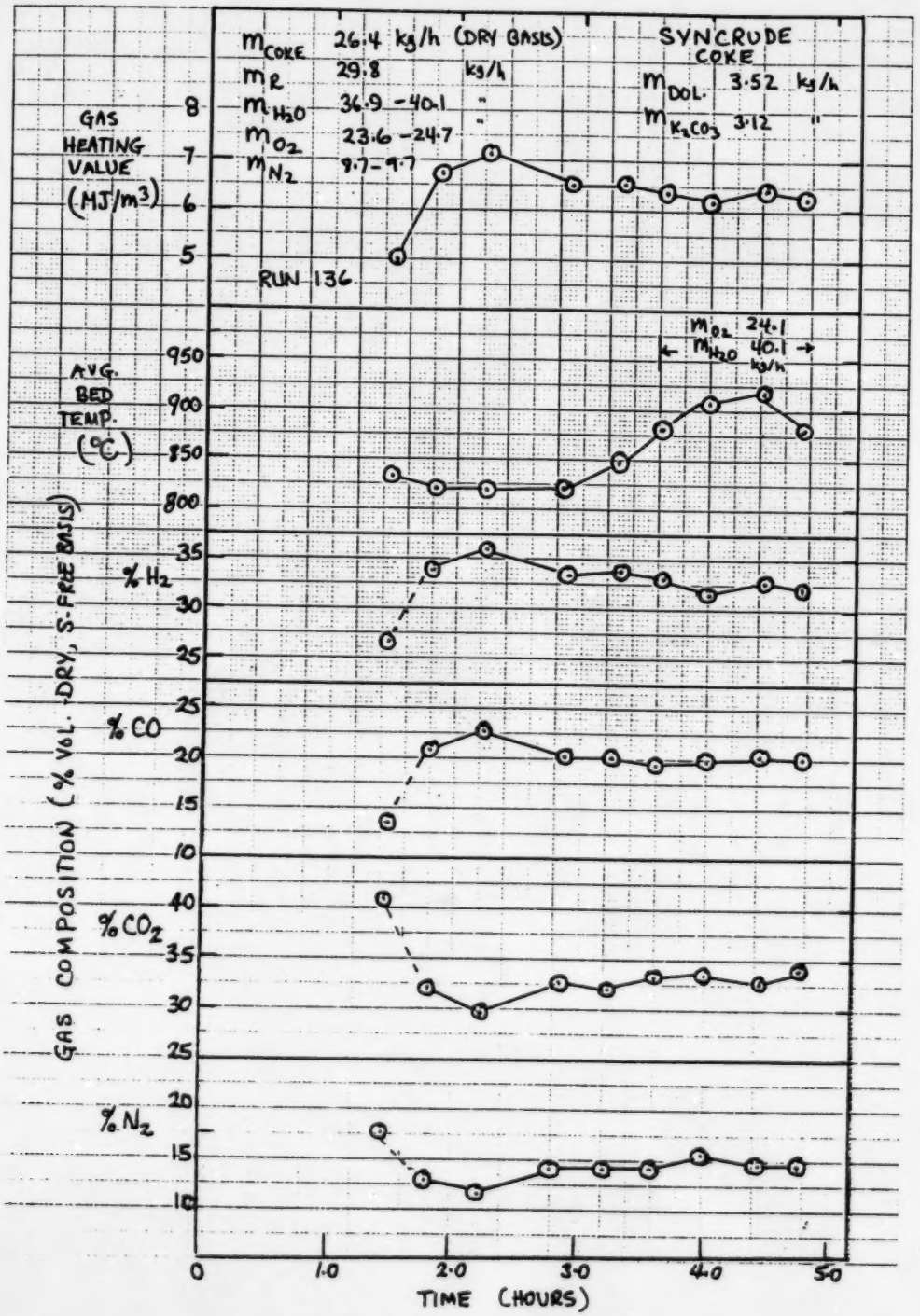


Fig. 14 Results of Extended Catalytic Run on Syncrude Coke

5.2.7 Overall Summary - Syncrude Tests

The present reactor system is not particularly well suited to gasification of cokes of particle size ~0.2 mm, since it was designed for coarse particles. Nevertheless some very useful results have been obtained.

(i) Gases of high heating values have been obtained at gasifier temperatures of ~950°C. Future work should concentrate on higher temperatures.

(ii) Carbon conversions are low in the present unit which operates at $U_o/U_t \simeq 75$ for the coke with a relatively inefficient cyclone system.

(iii) Addition of catalysts such as K_2CO_3 has a marked effect on improving performance of the gasifier with Syncrude coke.

(iv) Use of a dolomite bed reduced ($H_2S + SO_2$) in the produced gas from about 6% to 0.3%. In 4 runs, the average S level was ≃0.04%, with about 0.55% of the feed sulphur reporting to the produced gas.

(v) Quality of gas, other than its sulphur content, is roughly the same for fluidized beds of silica, coke or dolomite.

5.3 Sulphur Balances

Sulphur measurements in the gas and solid products are relatively difficult to make. In the gas, values below 0.5% H_2S are uncertain, and problems of dissolved SO_2 in any condensed water during gas sampling contribute to uncertainties. Where the gasifier bed at the end of the experiment consists of silica or coke, sulphur is readily determined. However dolomite injection or initial dolomite beds sometimes led to refractory sulphur species being formed, which gave no clear signals during the Leco sulphur analysis. Presumably a catalyst would help, although this analytical problem was not addressed in the current work. Tables 11 and 12 summarize the sulphur flows and balances. Bed sulphur levels as high as 11.5% were measured in some dolomite gasification runs, where dolomite was either the initial bed material or was co-fed with coke. As discussed in sections 5.1 and 5.2, in the case of no sorbent or catalyst, the sulphur reports primarily to the gas.

Because of the above mentioned analytical difficulties, sulphur balances did not close in all runs. In three cases an apparent large excess of sulphur is given in the gas, due undoubtedly to gas analysis problems. In five dolomite bed runs, unaccounted for sulphur is attributed to the bed material as no signal could be obtained in the Leco analyzer.

TABLE 11: Sulphur Analyses in Coke Gasification

RUN NO.	% SULPHUR (WT.) IN SOLIDS			% SULPHUR (VOL.) IN GAS	
	BED SAMPLE	CYCLONE I	CYCLONE OVERFLOW DRUM	H_2S	SO_2
117	4.07	5.33	4.58	1.27	0.00
118	2.71	6.62	6.57	0.71	0.032
119	10.40	10.70	6.95	0.13	0.010
120	9.48	9.29	11.80	0.35	0.014
121	6.84	7.83	NOT FOUND	0.93	0.019
122	4.91	6.22	6.57	1.27	0.00
123	* 0.92	6.37	6.27	0.78	1.33
124	3.26	5.99	6.08	0.58	4.24
125	NOT FOUND	6.25	5.86	5.92	3.47
126	1.89	6.53	5.35	1.59	0.19
127	NOT FOUND	5.06	5.40	3.06	0.01
128	1.02	5.19	4.16	3.74	0.05
129	* 24.17	6.32	6.73	0.07	0.01
130	11.50	6.00	5.63	0.26	0.003
131	* 3.96	4.94	6.21	0.25	0.02
132	* 14.52	5.44	5.06	0.05	0.00
133	* 5.80	6.14	5.42	0.03	0.03
134	* 29.24	5.01	5.68	0.02	0.00
135	10.50	6.25	6.89	0.006	0.00

* VALUE CALCULATED BY DIFFERENCE

TABLE 12: Sulphur Balances in Coke Gasification

		RUN NO.	SULPHUR INPUT (kg)			SULPHUR OUTPUTS (kg)				UNACCOUNTED SULPHUR * (kg)
			COKE FEED	BED MATERIAL	CYCLONE CHARGE	BED CHAR	CYCLONE #1 CATCH	CYCLONE OVERFLOW DRUM	FLUE GAS	
SUNCOR COKE		117	5.99	1.52	0.0	1.70	0.38	0.65	4.14	-0.65
	DOLOMITE	118	3.32	1.33		1.03	0.63	0.43	1.49	-1.08
		119	6.18	0.98		4.45	1.34	1.24	0.44	+0.31
		120	7.32	4.54		4.66	1.74	3.20	1.81	-0.44
	K_2CO_3	121	4.42	3.36		1.65	1.19	0.72	2.63	-1.58
		122	3.13	2.41	0.0	1.69	0.55	0.25	2.84	-0.21
SYNCRUDE COKE		123	6.30	0.0	0.0	† 0.35	1.36	2.10	2.49	—
		124	7.00		0.0	1.98	0.64	2.34	2.98	+0.93
		125	7.97		0.0	0.0	1.86	2.12	14.8 (?)	+ 10.8 (?)
		126	9.08		0.82	1.22	1.85	1.73	3.56	- 1.54
	K_2CO_3	127	6.50		0.50	0.0	1.09	0.08	8.77	+3.93
		128	9.14	0.0	0.89	0.57	0.69	1.25	19.57(?)	+12.09 (?)
	DOLOMITE	129	5.66	2.40	0.64	† 4.26	1.56	2.74	0.16	—
		130	12.83	2.57	0.77	3.41	1.43	7.22	0.56	-3.05
		131	4.50	0.0	0.72	† 2.88	0.73	1.17	0.44	—
		132	5.19		0.86	† 3.78	1.20	0.49	0.09	—
		133	8.00		0.54	† 1.34	1.73	5.42	0.05	—
		134	8.84		0.54	† 5.29	0.84	3.20	0.05	—
		135	20.13	0.0	0.93	4.87	1.59	10.66	0.05	-3.89

† CALCULATED BY DIFFERENCE

* SULPHUR OUTPUT - SULPHUR INPUT

5.4 Mathematical Modelling by Kinetics-Free Models

Two types of mathematical models are being investigated for prediction of gasifier performance and scale-up - the kinetics-free (equilibrium) model for prediction of final gas composition, and the two-region spouted bed model to predict composition profiles within the reactor, and to show effects of independent design variables on scale-up (Z. Haji-Sulaiman, M.A.Sc. Thesis, Dept. Chem. Eng., U.B.C. 1984). In this report some results of the kinetics-free model are reported for the coke gasification runs. This work was carried out by Dr. C.J. Lim.

In the kinetics-free model we assume that the exit gas composition of the gasifier is determined solely by stoichiometric and thermodynamic constraints. The following specific assumptions are made in the model development:

a) All feed oxygen is consumed

b) Carbon conversion is given (from experimental measurement)

c) Exit gases from the gasifier contain H_2, CO, CO_2, CH_4, H_2O and N_2, and are in water_gas shift and methanation equilibrium at the average gasifier temperature.

The model consists of a series of elemental mass balance equations for C, O, H, and N, the equilibrium equations of the water_gas shift and the methanation reactions, and Dalton's law. They are summarized as follows:

1) The equilibrium equations

$$\text{For water-gas shift: } K_I = \frac{(y_{H_2})(y_{CO_2})}{(y_{CO})(y_{H_2O})} \qquad (3)$$

$$\text{For methanation: } K_{II} = \frac{(y_{CH_4})(y_{H_2O})}{(y_{CO})(y_{H_2})^3 p^2} \qquad (4)$$

where the y are the mole fractions and p is the total pressure of the system (1 atm for our case). K_I and K_{II} are the corresponding equilibrium constants given by the following expressions:

$$K_I = 0.0265 \text{ Exp}(3956/T)$$

$$K_{II} = 6.7125 \times 10^{-14} \text{ Exp}(27020/T)$$

where T is the average gasifier temperature.

2) The elemental mass balance equations

For H_2: $(2y_{CH_4} + y_{H_2} + y_{H_2O})n = n_{H_2}$ (5)

For O_2: $(y_{CO}/2 + y_{CO_2} + y_{H_2O}/2)n = n_{O_2,F}$ (6)

For C: $(y_{CH_4} + y_{CO} + y_{CO_2})n = Xn_{C,F}$ (7)

For N: $ny_{N_2} = n_{N_2,F}$ (8)

where n_{H_2F}, $n_{O_2,F}$, $n_{C,F}$ and $n_{N_2,F}$ are the number of moles of hydrogen, oxygen, carbon and nitrogen fed to the gasifier, n is the total molar flows in the exit gases, and X is fraction of carbon converted to gases.

3) Dalton's Law

$$y_{CO} + y_{CO_2} + y_{H_2} + y_{H_2O} + y_{N_2} + y_{CH_4} = 1 \qquad (9)$$

For a given gasification experiment, $n_{H_2,F}$, $n_{O_2,F}$, $n_{C,F}$, $n_{N_2,F}$, T and X are known. K_I and K_{II} can be calculated from T. The equations (3) to (9) can be solved by a nonlinear equation routine on the UBC computer to yield exit gas compositions, y_{CO}, y_{CO_2}, y_{H_2}, y_{CH_4}, y_{H_2O}, and y_{N_2}, as well as n, the total molar flow. The H_2/CO molar ratio and GCV of the exit gases can be

calculated. Comparisons between the experimental and calculated values of H_2/CO molar ratio and GCV for Suncor and Syncrude cokes gasification runs are shown in the following figures.

Figure 15 shows reasonably good agreement (~±15%) between the measured heating values of the gas, and those predicted by the model for both the Syncrude and the Suncor cokes. The molar ratio of H_2/CO predicted vs. measured is shown in Figure 16. The predictions seem better for Syncrude than for Suncor cokes, and it appears that measured H_2/CO ratios are somewhat below those predicted particularly for Suncor coke, where in the worst cases the experimental values are about 30% below those predicted.

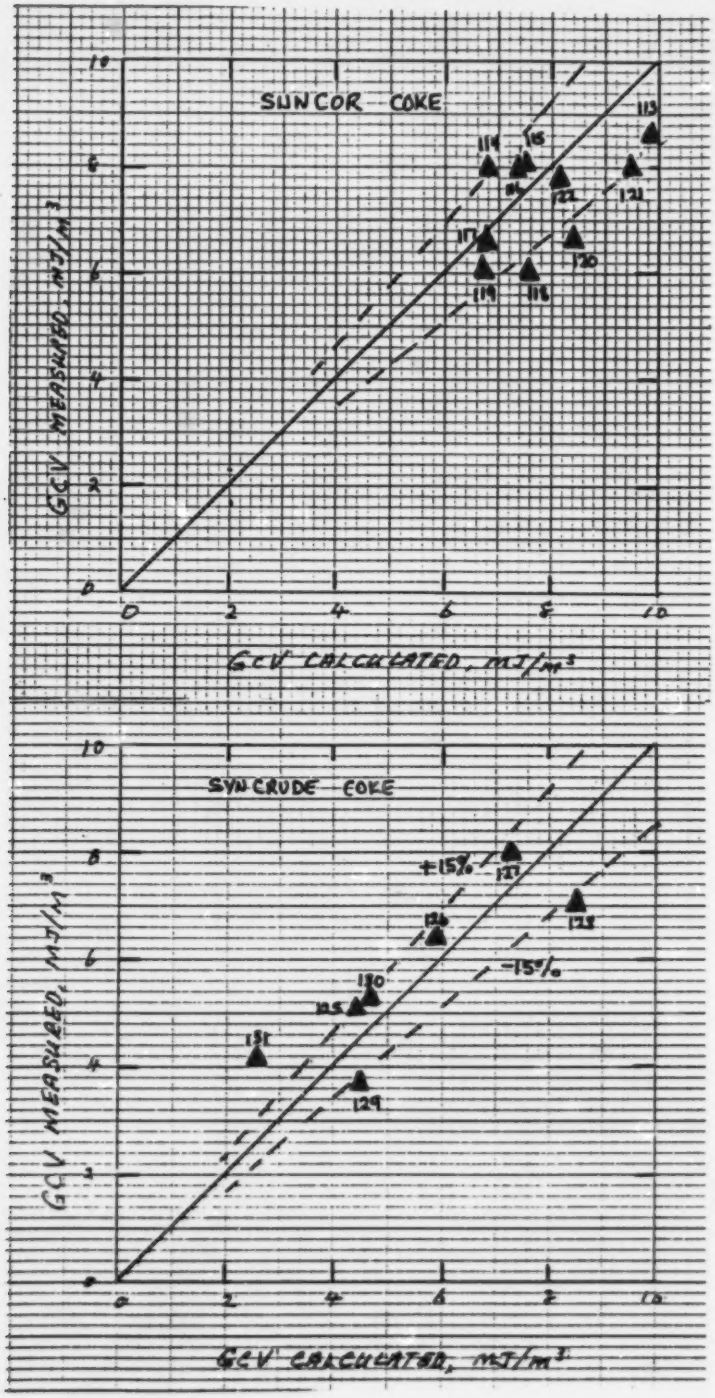


Fig. 15 Measured Versus Predicted Gas Heating Values for Gasification of Suncor and Syncrude Coke.

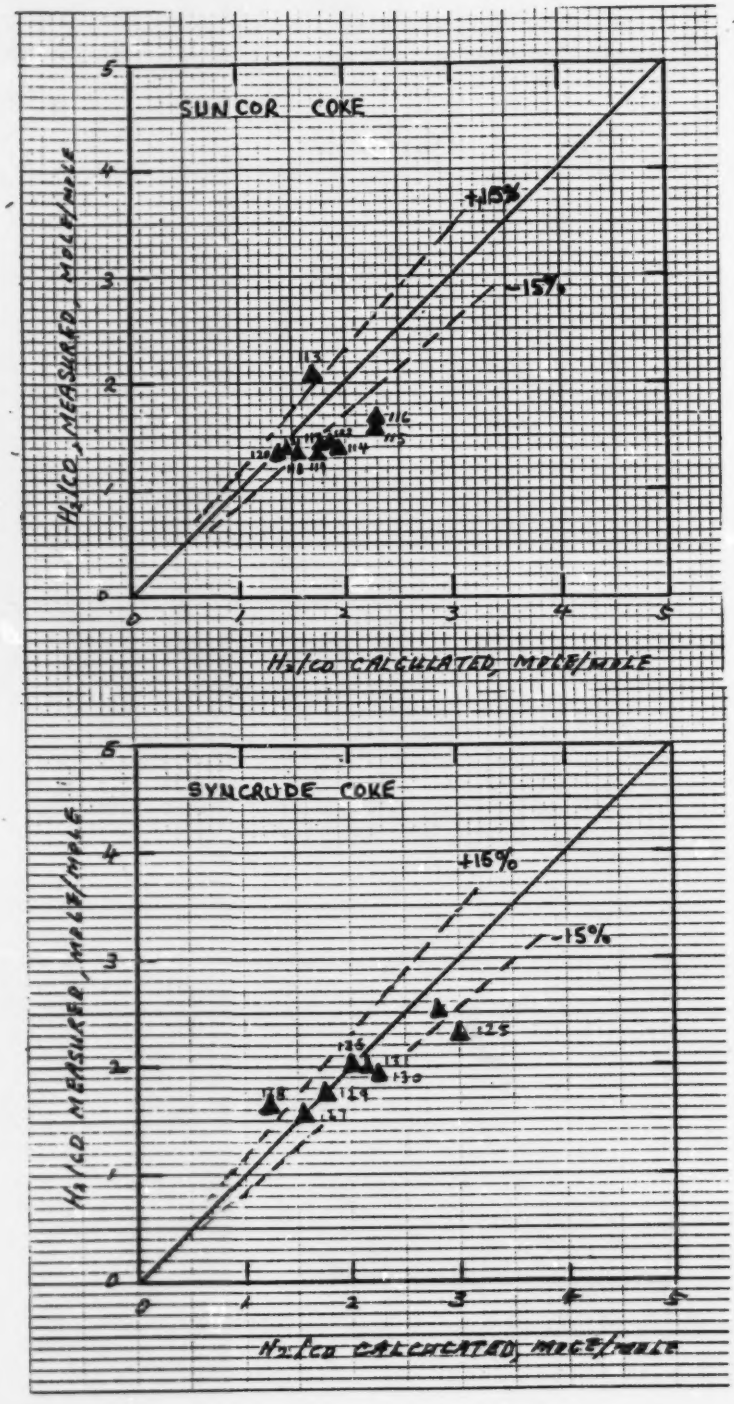


Fig. 16 Measured Versus Predicted H_2/CO Ratios for Gasification of Suncor and Syncrude Coke

5.5 Kinetic Study

Ph.D. candidate Quoi Nguyen has constructed a stirred bed kinetic unit (Fig. 17) to follow the rates of the steam-coke, CO_2-coke and sulphur evolution and capture reactions. A batch of 150 g. coke is placed in the reactor with or without dolomite and the system heated to reaction temperature in nitrogen. The steam flow is then started and the gas composition followed with time. Figures 18 and 19 show plots of the gas composition with time for initial tests on Suncor coke, with and without dolomite present. The influence of the dolomite on the H_2S level is apparent with a gas of about 10,000 ppm(v) H_2S being generated without dolomite, and about a few hundred ppm with the dolomite. The reduction in H_2S level is thus about 97%. The fractional conversion of the carbon in the coke is also shown in these figures. The carbon gasification rate is readily determined from the slopes of the curves.

This work is in its early stages, and the objects are to determine

(i) the rates of H_2S evolution during gasification of coke with steam and CO_2

(ii) the factors governing the sulphur adsorption onto dolomite and limestone

(iii) the relative reaction rates of H_2O-C and CO_2-C for oil sand cokes.

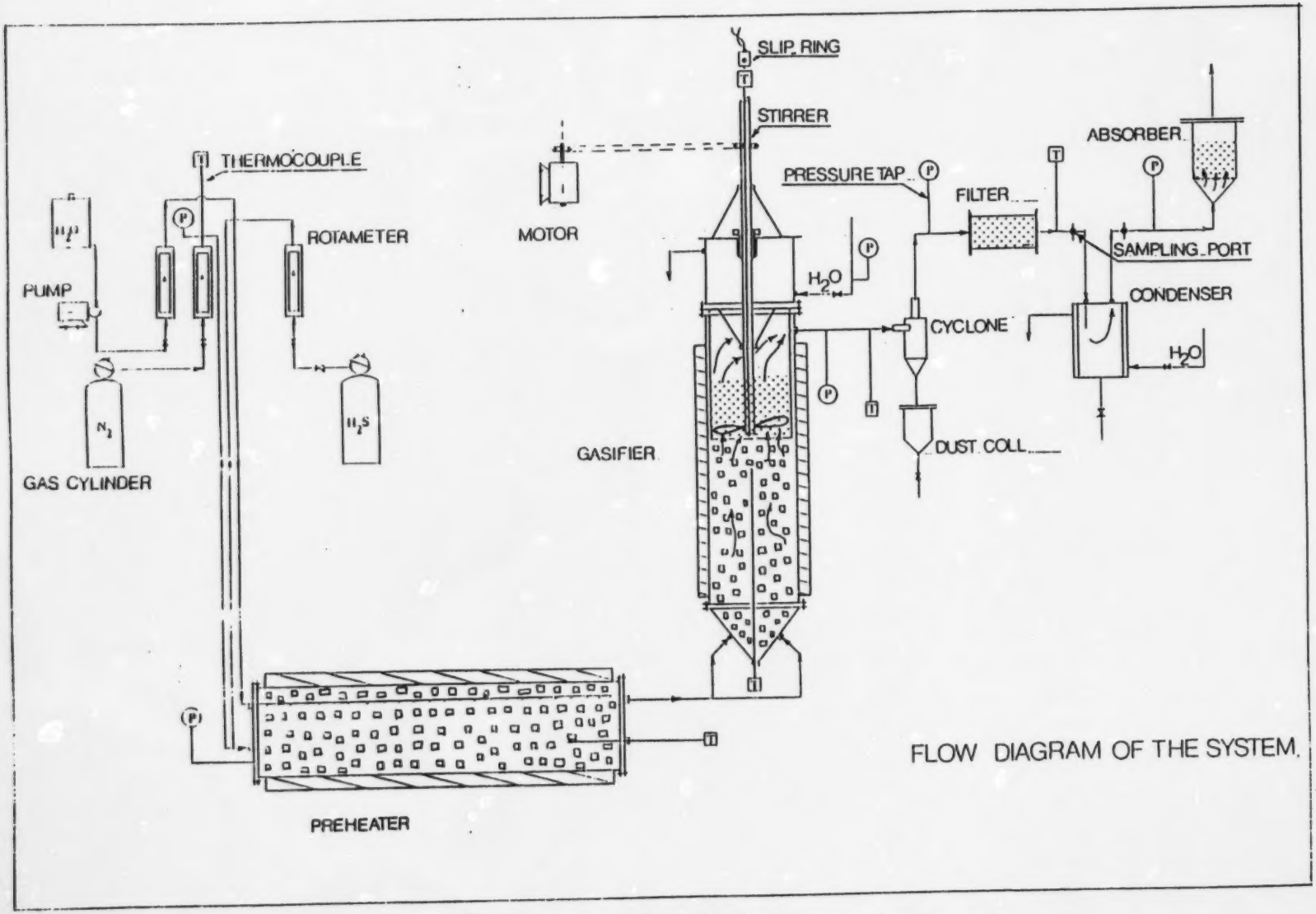


Fig. 17 Schematic Diagram of Kinetic Unit

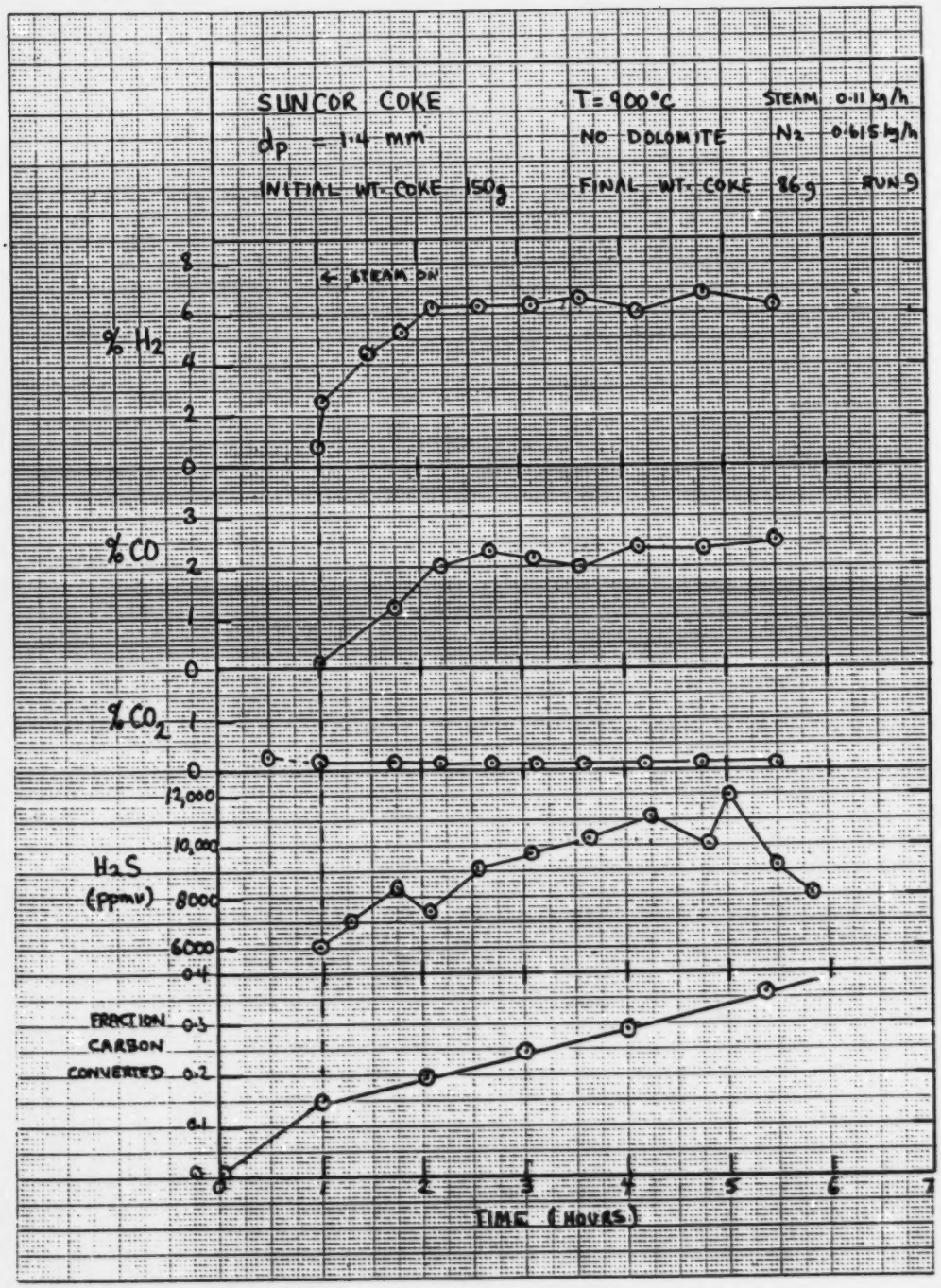


Fig. 18 Results of Kinetic Run 9

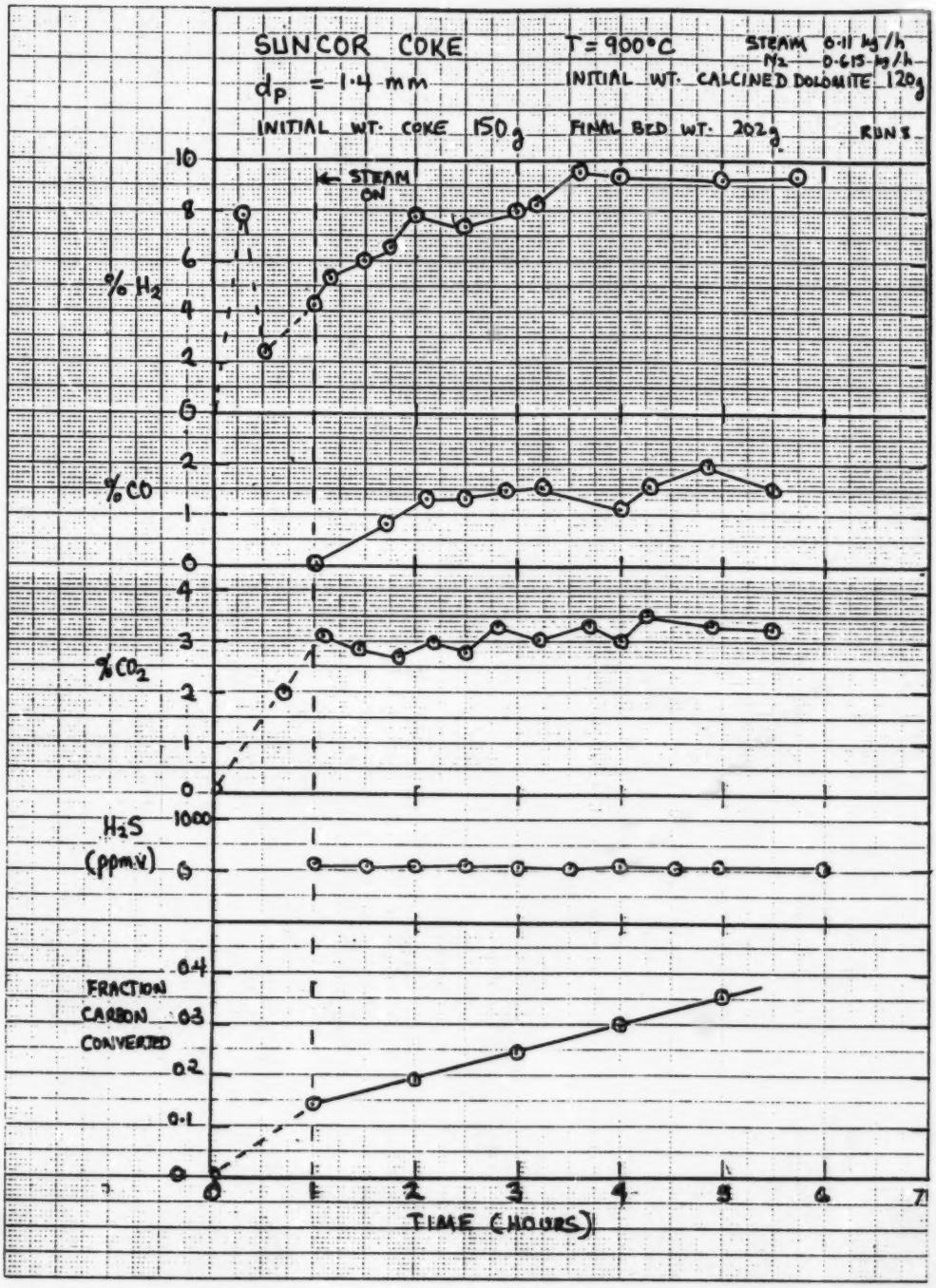


Fig. 19 Results of Kinetic Run 8

6. Conclusions and Further Work

Experimental and computational work carried out in the present research contract has shown that

1. Suncor coke of particle size 1.5 mm can be readily gasified by a steam-oxygen mixture in a spouted bed to yield a gas of about 33-38% H_2, 22-28% CO and 38-44% CO_2 on a dry basis at carbon conversions up to 94%. Heating values of the gas reached 8.8 MJ/m^3 at H_2/CO ratios of about 1.4. K_2CO_3 catalyst addition increased the extent of carbon conversion and steam decomposition at temperatures some 50-100°C lower than the 930°C typical of non-catalytic runs. Co-feeding of coke and dolomite reduced the sulphur content of the produced gas.

2. Syncrude coke of particle size 0.2 mm gasified at temperatures up to 980°C in a fluidized bed yielded lower carbon conversion levels and higher CO_2 contents than did Suncor coke. Gas heating values to 8 MJ/m^3 on an N_2-free basis were achieved with gas compositions of about 28-38% H_2, 16-24% CO and 36-55% CO_2. Results suggest that to reach carbon conversions in excess of 80% in the present apparatus will require temperatures in excess of 1000°C. K_2CO_3 catalyst addition raised the carbon conversion to this level at temperatures of about 880°C. Gasification in dolomite beds resulted in substantial reduction of off-gas sulphur content from about 24,000 ppmv to around 1000 ppmv. The effects of O_2/coke ratio and recycling of cyclone char on heating values and carbon conversion were demonstrated.

3. Outlet gas H_2/CO ratios and heating values are adequately predicted using an equilibrium model consisting of the water-gas shift and methanation reactions.

4. Studies begun in a small kinetic unit show promise to quantify the kinetics of sulphur release, carbon gasification and in-situ sulphur capture

by limestone and dolomite.

Further work should be addressed at raising the carbon conversion with Syncrude coke in the absence of catalyst. Modification to the cyclone system for virtual total recycle is required, coupled with operation at temperatures of about 1000°C. Changes are being made to the UBC pilot gasifier which will improve handling of fine particles, and their recycle to the gasifier. The kinetic information being generated in the small kinetic unit coupled with recent results by Furimsky(4), will be entered into the kinetic model of the UBC spouted bed gasifier and results compared with measured internal gas composition profiles.

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2. A.M. Squires, R.A. Graff and M. Pell, "Desulphurization of fuels with calcined dolomite." A.I.Ch.E. Symp. Ser. No. 115, 67, 23-34 (1971).

3. J.S.M. Botterill and Y. Teoman, "Fluidized bed behaviour at elevated temperatures." In Fluidization, J.R. Grace and J.M. Matson (eds.), Plenum Press, 93-100 (1980).

4. E. Furimsky, "Gasification reactivities of cokes derived from Athabasca bitumen." Fuel Processing Technology 11, 167-182 (1985).

APPENDIX A

TABLE A-1: Analysis of Dolomites

Major Components(% wt.)*	Dolomite Sand	Granular Dolomite
CaO	31.1	35.3
MgO	22.0	25.0
SiO_2	1.73	8.34
Al_2O_3	0.23	0.95
Fe_2O_3	0.20	0.98
Na_2O	0.10	0.10
K_2O	0.06	0.30
SO_3	0.02	1.65
Loss on ignition	44.7	27.9

* By plasma spectrographic method.

Note: Granular dolomite used as co-feed in spouted bed and fluid bed runs.
Dolomite sand used as bed material in fluid bed runs.

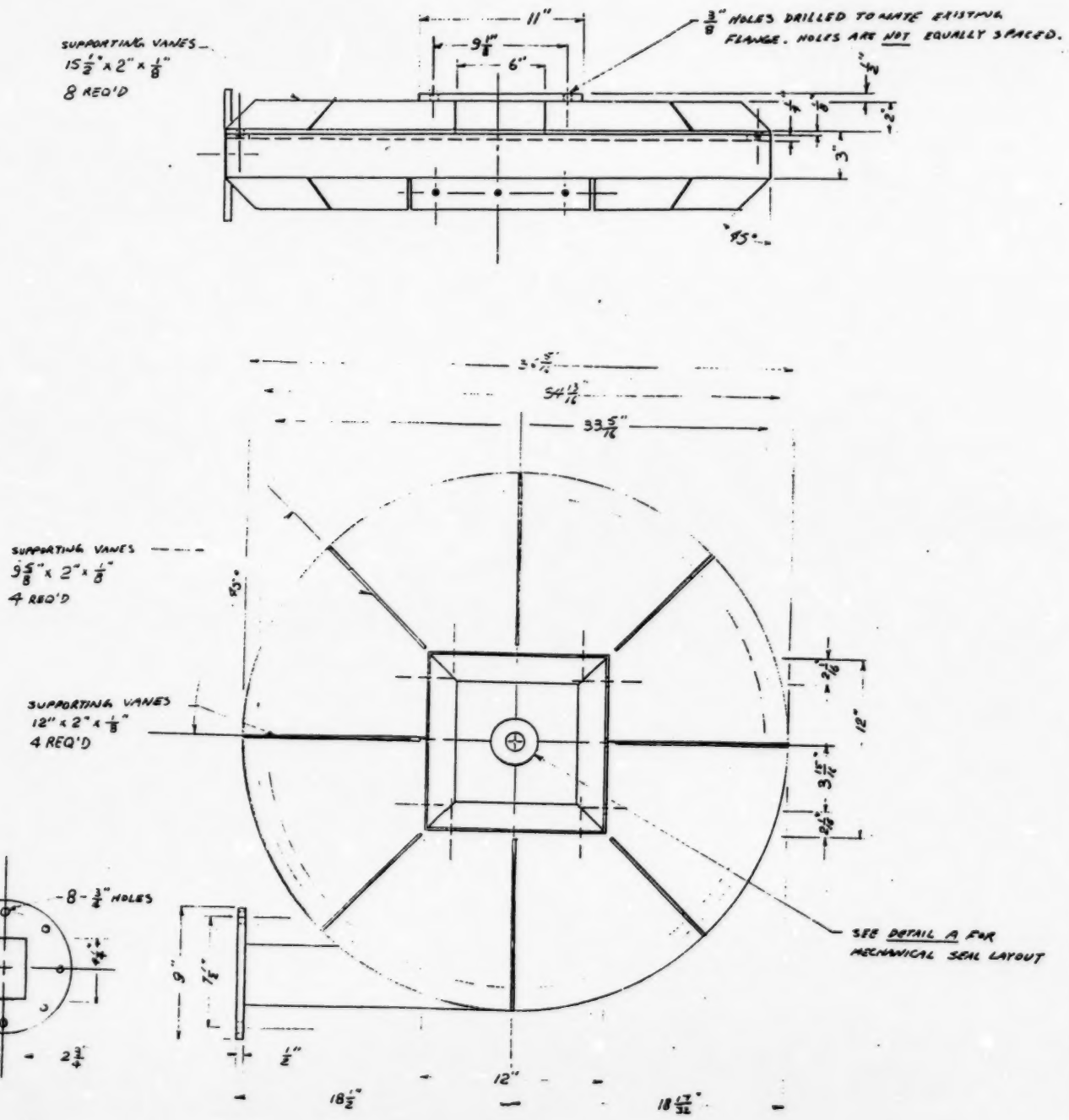


Fig. A-1 Gas Exhaust Fan

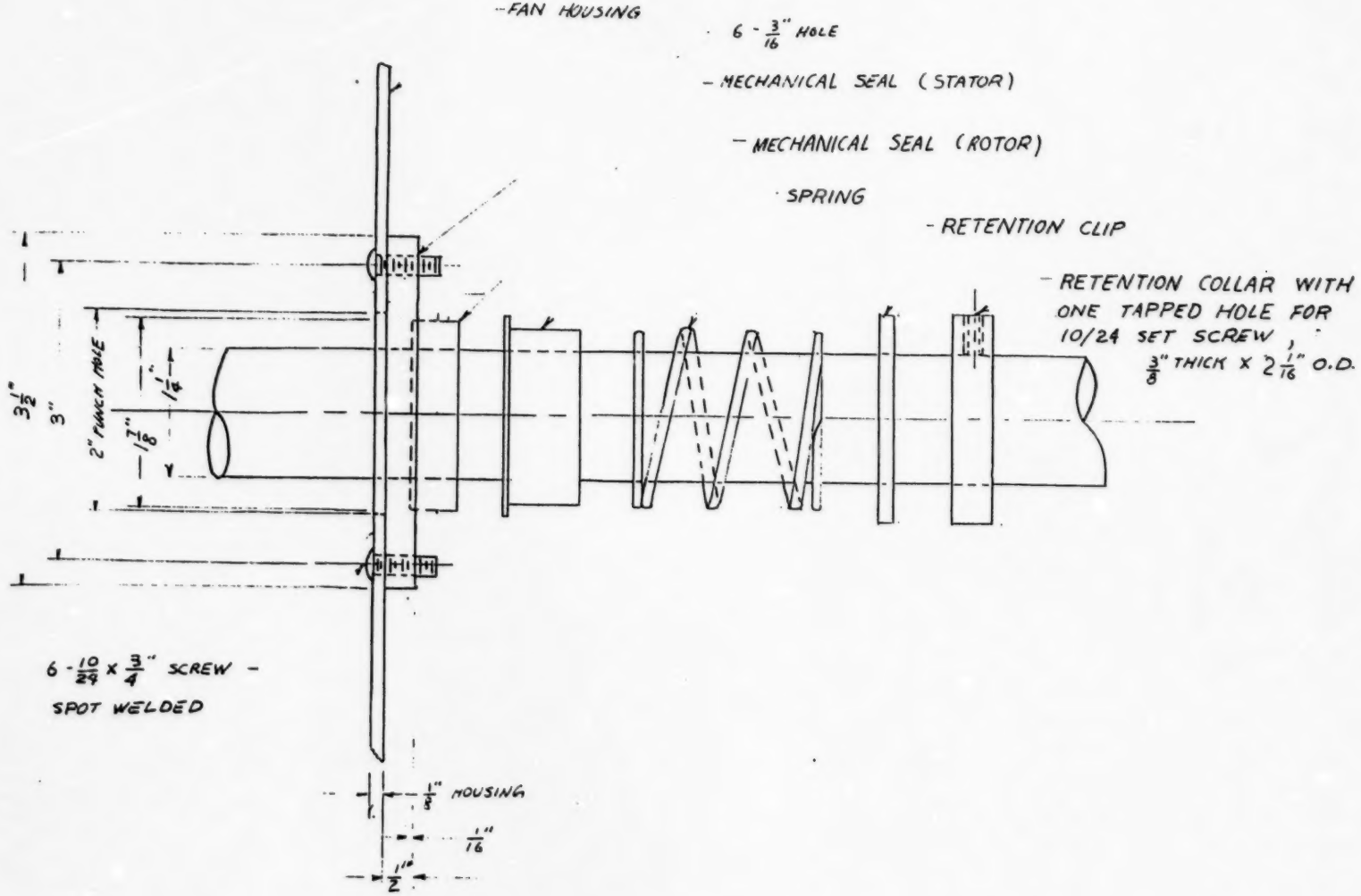


Fig. A-1 DETAIL A :- MECHANICAL SEAL ASSEMBLY

RS 232 PIN NO.		RS 232 PIN NO.
DATA TRANSMIT 2	———	3 DATA RECEIVE
DATA RECEIVE 3	———	2 DATA TRANSMIT
GROUND 7	———	7 GROUND
DORIC 235 SIDE		COMPUTER SIDE.

RS232 CABLE CONNECTION BETWEEN DORIC 235 AND APPLE II+ COMPATIBLE COMPUTER.

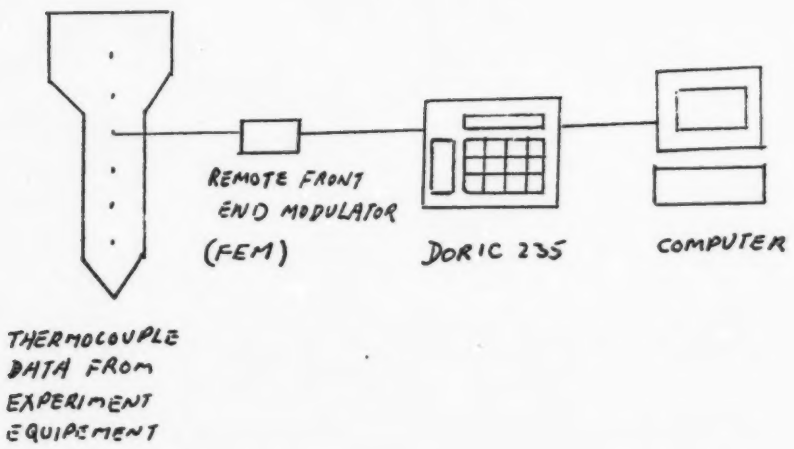
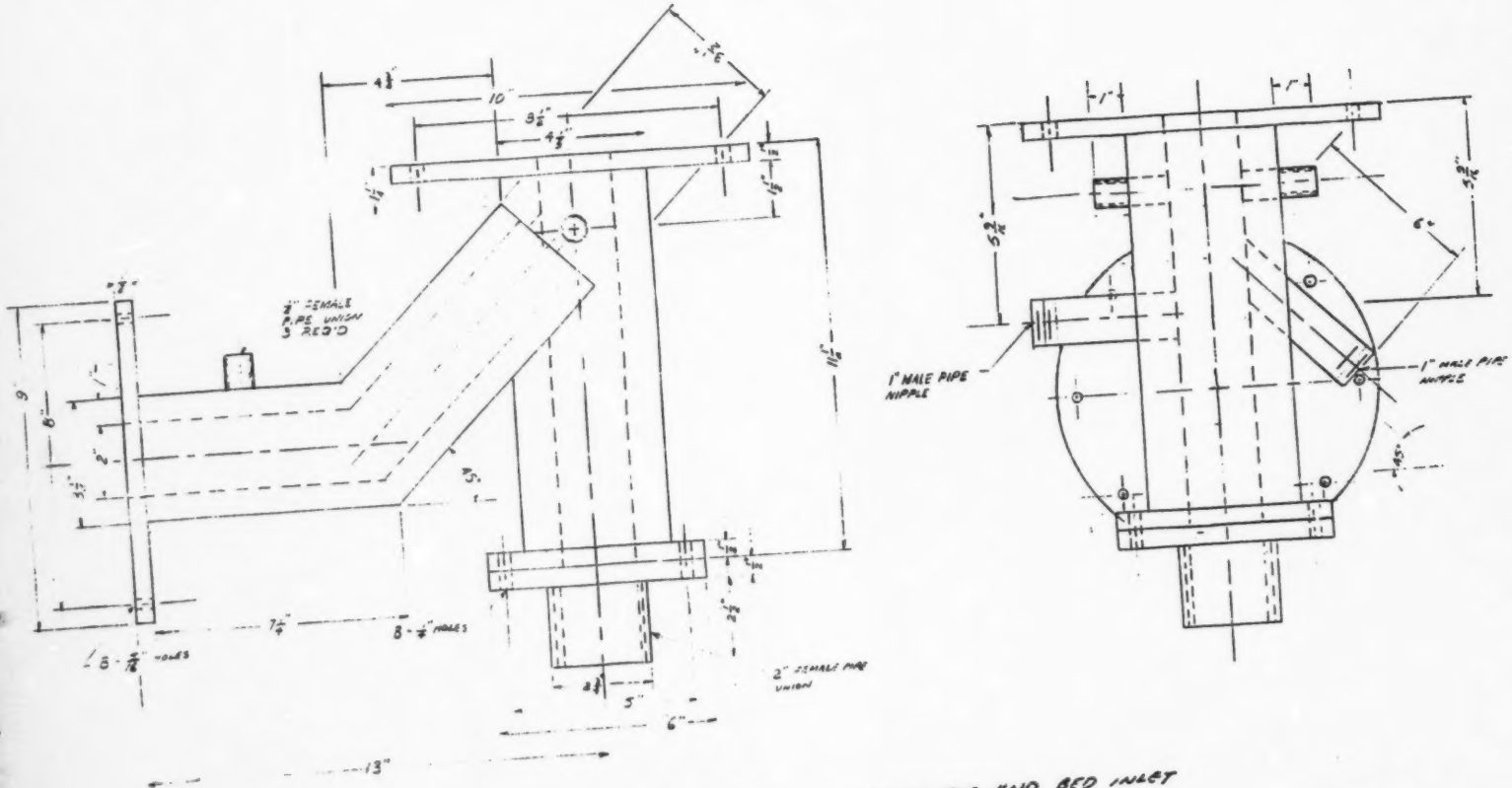


Fig A-2 THERMOCOUPLE DATA HOOK-UP TO DORIC 235 DATALOGGER AND APPLE COMPATIBLE COMPUTER.



REFRACTORY LINED PIPE SECTION LOCATED BETWEEN THE PREHEATER AND BED INLET

Fig A-3